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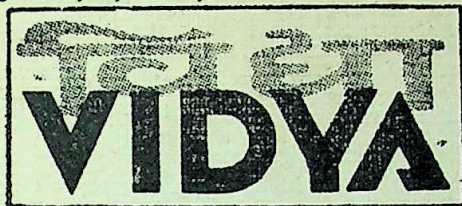
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CONTENTS

(*ii*)

STUDIES OF AMINOACID COMPOSITION AND PROTEIN CONTENT OF THE MUCUS OF SP. *LAEVICAULIS ALTE* (FERUSSAC)

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Abstract

Protein content and aminoacids in mucus of *Laevicaulis alte* have been studied. Protein content in mucus is ranged between 3.048% to 4.520%. Seven aminoacids were identified in the mucus protein

Introduction :

Mucus secretion is a very characteristic phenomenon observed in most of the gastropods. The mucus is secreted by the mucus cells of the supra-pedal gland, and of the caudal gland, if present, and practically by the whole body surface. The distribution and histochemical study of such cells have been reported in *Arion ater* by Chetail and Binot (1967) and Wondrak (1968, 1969). Further the chemical analysis of mucus in *Halix pomatia* and *Oxychilus alliarius* has been worked out by Burton (1965), and Fantain and Balognari (1964) and Lloyed (1969) respectively. Most of the work on protein and aminoacid content of mucus is done on Amphibia and Mammals.

Present investigation was undertaken with a view to finding out aminoacid present in protein of mucus by paper chromatographic method, and qualitative determination of protein contents.

Material and Method :

Laevicaulis alte was collected from the garden where there is abundance of moisture. They were repeatedly washed with distilled water, and the surface moisture was removed by mild pressing with filter paper. The animal was stimulated with a pointed forcep to secrete the mucus. The mucus collected was then weighed.

The protein content was determined by micro-Kjeldahl method for Nitrogen. For the study of aminoacids present in protein of mucus, 200 mgs. of mucus was taken in a flask to which 3 ml. of 6 N HCL was added. The mixture was hydrolysed under 15 lb. pressure in an autoclave for 45 mins Hydrolysate was filtered and evaporated to dryness on a water bath. The residue was dried over Sodium hydroxide in a vaccum desiccator for over night Then 20 ml. of 80 % ethyl alcohol and 60 ml. of chloroform were added, evaporated to dryness and finally dissolved in 10% isopropanol.

Complete separation and identification of aminoacids was achieved by one dimensional paper chromatographic technique. The aminoacids were separated by descending chromatography on $11'' \times 11''$ filter paper using the solvent system n-butanol–acetic acid–water (60 : 15 : 25 v/v). The chromatography was allowed to develop for 6 hrs. at room temperature. The chromatogram paper was dried, 1% ninehydrin solution in n-butanol was sprayed on it, and subsequently the paper was dried at 60' C for 15 mins.

Result and Discussion :

The result of ten analysis by the micro-Kjeldahl methods carried out with *Laevicaulis alte* showed that the protein content ranged from 3.048% to 4.520% with an average of 4,064% $\pm$ 0.161 of protein. The reference of the protein content of mucus in gastropods is of snail *Oxychilus alliarius,* which has been reported by Lloyed (1969). According to him, the mucus consists of 6.8% solids of which 77% was protein and the remainder consists of inorganic matter. The protein content of mucus in *Oxychilus alliarius* comes to 5.23%.

The results presented from the chromatograph indicates that the protein present in mucus consists of the following aminoacids : (1) Lysin

Paper chromatogram of protein of mucus of *Laevicaulis alte*. Developing system : n-butanol–acetic acid–water (60 : 15 : 25 v/v) and ninhydrin spray.

(Rf. 0.08) (2) Aspartic acid (Rf. 0.15) (3) Threonine (Rf. 0.26) (4) Alanine (Rf. 0.32) (5) Tryptophan (Rf. 0.43) (6) Valine (Rf. 0.55) (7) Leucine (Rf. 0.69). Aspartic acid, threonine and alanine were present in slightly larger quantities than the other aminoacids, but this difference does not seem to be significant. With reference to the analysis of aminoacids from the mucus protein 16 such aminoacids have been reported from the mucus of snail *Lymnea turncatula* by Wilson (1969). Scheer and Florkin (1971) reported that peptied moiety of mucus was high in aspartic acid and glutamic acid.

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STIMULATION OF IMBIBITION, GROWTH AND ASCORBIC ACID METABOLISM OF EMBRYO-AXIS OF *ARACHIS-HYPOGEA* BY LOW TEMPERATURE AND GROWTH REGULATORS

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Abstract

The excised embryo-axes of *Arachis hypogea var. A. H.* 334 (*Junagadh*) were cultured in different media containing sucrose, indole-3-acetic acid, gibberellin and their various combinations at two different temperatures, viz. low temperature (5-7° C) and room temperature (25-27° C). Growth, differentiation, water uptake as well as the concentration of the endogenous ascorbic acid and ascorbic acid utilization were determined at regular time intervals.

Growth regulators such as IAA and GA act as catalyst in the biosynthesis of ascorbic acid, simultaneously the utilization of ascorbic acid is also appreciably increased. Addition of 1 % sucrose to the medium containing above growth regulators not only accelerates the ascorbic acid content but also steps up its utilization. Enhancement of ascorbic acid as well as its increased utilization are correlated with rapid imbibition of water, growth and differentiation.

The role of ascorbic acid in growth is discussed and it was postulated that auxin and gibberellin catalyzes the biosynthesis of ascorbic acid and that ascorbic acid helps in the synthesis of nucleic acid, protein, enzyme proteins and cell-wall constituents by creating a favourable redox balance and thereby enabling the process of cell division and enlargement to proceed at a faster rate which will determine the pattern of plant development.

Introduction

It was suggested earlier that auxins and gibberellins influenced the growth of tissue explants by catalyzing the biosynthesis of ascorbic acid, which being an universal constituent of the redox system of plants acted as the growth regulator (Chinoy et. al. 1958, 1961, 1965, 1967, 1971; Chinoy and Nanda, 1959).

Evidence presented in the paper shows that the concentration of AA as well as its utilization are correlated with the processes of imbibition and growth of the embryo-axis of *Arachis hypogea* and that the biosynthesis of AA is catalyzed by auxin and gibberellin.

Material and Method

Ten embryo-axes of similar size and weight of *Arachis hypogea*, var. *A. H.* 334, *Junagadh* were placed in each petridish (9 cm. diameter) lined with sterilized filter paper at room temperature (25-27° C) as well as at low temperature (5-7° C) in complete darkness. Following media of growth were used for this experiment :

1. Distilled water
2. Sucrose 1%
3. GA 1 mg/l.
4. IAA 1 mg/l.
5. GA + Sucrose
6. IAA + Sucrose
7. GA + IAA + Sucrose.

(Each constituent in media 5, 6 and 7 was maintained at the same concentration as in 2, 3 and 4 respectively.)

Two embryo-axes were removed after every 24 hours and their length and weight were determined. These were washed with distilled water for estimations of ascorbic acid (AA) and ascorbic acid utilization (AAU) separately, titrimetrically with 2, 6-dichlorophenol-indophenol (Chinoy, 1962). The above process was repeated for 48, 72 and 96 hours at room temperature while at low temperature the estimations and measurements were done at 48-hourly intervals upto 192 hours.

Results

This being a complex experiment the data has been grouped in different ways. The effects of vernalization and substrates are presented in fig. 1 while those of vernalization and germination period in fig. 2. Exogenous application of sucrose and GA combined with sucrose give accelerating effect on imbibition at room temperature. GA and IAA when combined with sucrose show accelerating effect on imbibition as compared to that in GA and IAA alone (Fig. 1). At low temperature differences are not well
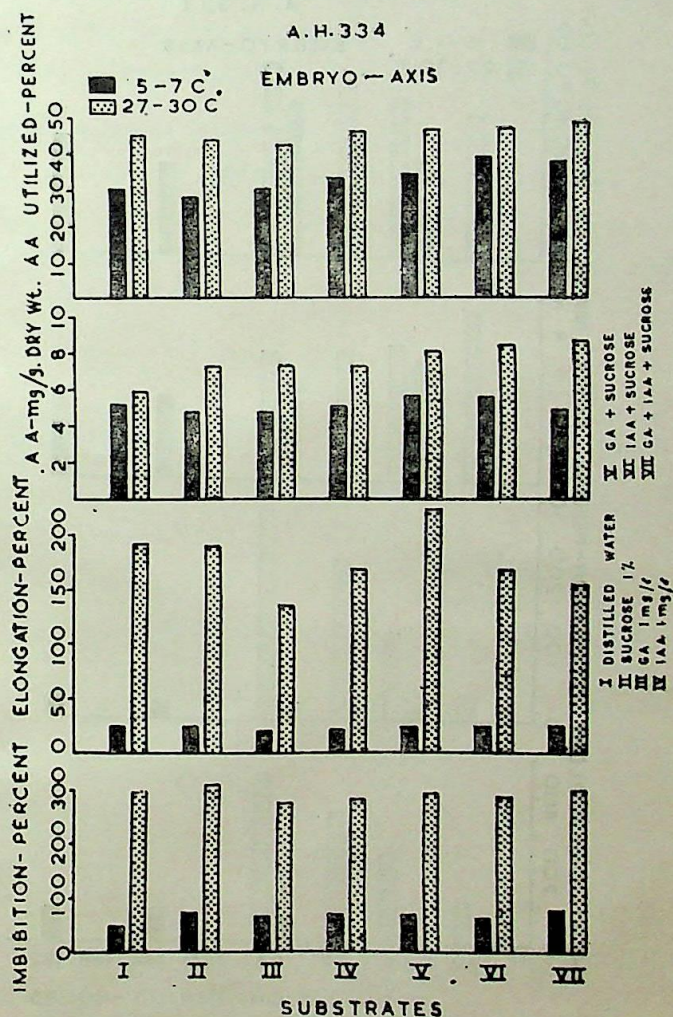
Fig. 1. Interaction of substrates and vernalization treatment

marked still substrates containing GA, IAA and sucrose show better growth as compared to that in other substrates.

Low temperature depresses the growth of the embryo-axis. At optimum temperature embryo-axis grow much faster than that in low temperature. Highest growth is registered in substrate 6 containing GA and sucrose (Fig. 1). It seems that GA and IAA combined with sucrose accelerate the elongation of embryo-axis as compared to that in GA and IAA alone. Growth is also accelerated in substrate 2 containing sucrose alone. At low temperature the effect of different substrates is not well marked.

During early hours of germination ascorbic acid content is generally high and it gradually decreases with the march of time (Fig. 2). At
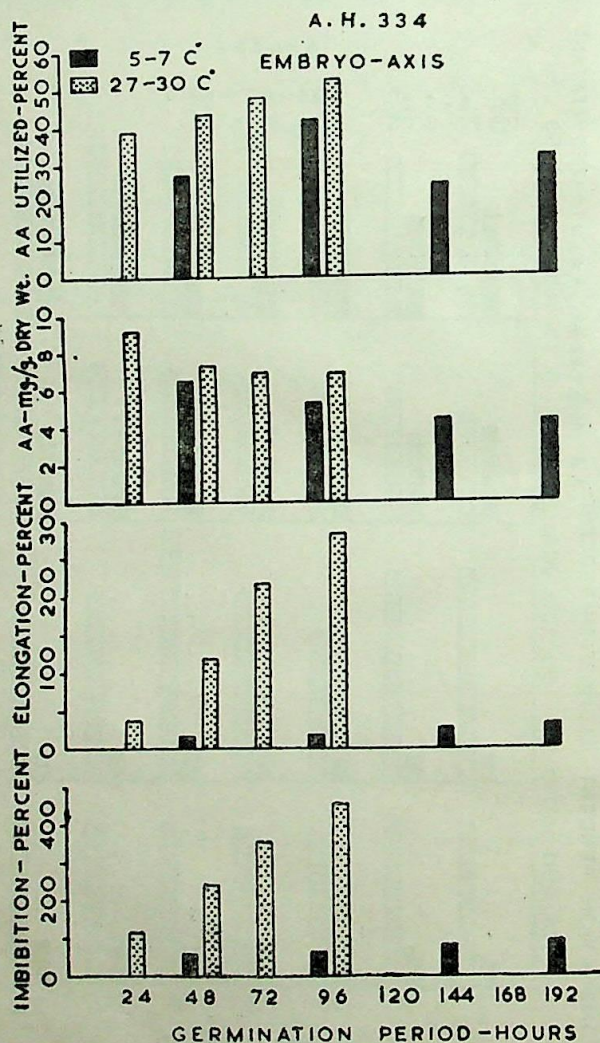
Fig. 2. Interaction of vernalization treatment and different periods of germination

optimum as well as at low temperature ascorbic acid content is generally higher in all substrates containing sucrose as compared to non-sucrose

substrates. At low temperature growth is arrested and consequently ascorbic acid content is comparatively higher. It appears that GA and IAA when combined with sucrose enhances ascorbic acid content as compared to GA and IAA alone.

Ascorbic acid utilization is less in the beginning and increases little after 96 hours of germination at optimum temperature. At low temperature enzyme activity increases upto 96 hours and then decreases. Enzyme activity is slightly increased in substrates containing sucrose as compared to that in non sucrose substrates. At low temperature substrates 5, 6 and 7 show higher utilization of ascorbic acid as compared to other substrates.

Analysis of variance of data of imbibition, elongation, ascorbic acid content and ascorbic acid utilization were carried out and presented in table 1 and 2. Temperature was highly significant in both the tables. Germination period was also found highly significant in the case of imbi-

TABLE 1

Analysis of Variance of Data of Imbibition, Elongation and Ascorbic Acid Content

Factors	Degree of freedom	Value of F		
		Imbibition	Elongation	AA content
Replicates	3	5.9	1.5	9.2
Substrates (S)	6	0.7	0.6	0.7
Germination period (GP)	3	45.7 S	2.3	1.8
Temperature (T)	1	349.9 S	15.3 S	19.2 S
S × GP	18	0.4	0.2	0.3
S × T	6	0.5	0.5	0.7
Error	186			
Total	223			

S significant at 1% point

TABLE 2

Analysis of Variance of Data of Ascorbic Acid Utilization

	Degree of freedom	Value of F
Replicates	3	2.6
Substrates (S)	6	4.6 S
Germination period (GP)	3	20.3 S
Temperature (T)	1	151.3 S
Enzyme activity (EA)	3	81.3 S
S × GP	18	1.1
S × T	6	0.9
GP × T	3	10.9 S
EA × GP	9	1.9
Error	843	
Total	895	

S significant at 1% point

bition and ascorbic acid utilization. In the case of ascorbic acid utilization substrates, enzyme activity as well as interaction between germination period and temperature were highly significant.

Discussion

The early production of ascorbic acid as well as its utilization in the embryonal axis lends support to the conclusion that ascorbic acid metabolism plays an important role in the initial germinative processes even during the first few hours after the start of imbibition of water. Further it has already been shown in the case of wheat, which has not got the same silicious coat as the barley, that with the imbibition of water ascorbic acid production and utilization starts in the embryo during early hours of germination (Chinoy and Nanda, 1959; Chinoy, et. al. 1967). These workers were also first to show that auxin (IAA) catalyzes the biosynthesis of ascorbic acid in germinating wheat embryos. Experimental data presented by Michniewicz and his coworkers (1966) also support the above mentioned findings. Moreover, Chinoy et. al. (1965, 1967) have also shown that

short duration incubation of root tips as well as coleoptile tips in substrates containing IAA and GA combined with sucrose enhances the biosynthesis of ascorbic acid as well as accelerates its utilization. This significant fact, which has also been previously observed by a number of workers not only in seeds and excised embryos but in isolated sections of different plant material (Chinoy and Nanda, 1959; Chinoy, et. al. 1957, 1961 1965, 1967; Chinoy, 1966: Michniewicz, 1960, 1966).

Addition of 1 per cent sucrose to the medium containing auxin and gibberellin augmented to a considerable extent not only the concentration of ascorbic acid but also increased its utilization, at the same time growth was increased (Chinoy, et. al. 1965, 1967; Shrinivasan and Wandrekar, 1950a). In 1 per cent sucrose AA might be synthesized endogenously from sucrose or from other carbohydrates. The experiments on Avena coleoptile section have proved that when different concentrations of sucrose (0.1 and 1.0 per cent) were used appreciable enhancement in linear growth of Avena sections over the non–sucrose series took place only in media containing 1 per cent sucrose. The enhancement in growth is not so well marked in the case of low concentration of sucrose viz. 0.1 per cent (Chinoy, et. al. 1957, 1961). Sucrose over and above acting as a food factor also serves as a precursor for the synthesis of growth regulatory substances. These findings were confirmed by studying the growth–auxin relationship by the method of enzyme kinetics as well as actual determination of ascorbic acid content in embryos and explants of plant organs (Chinoy et. al. 1965).

From the above evidences it has become increasingly clear that AA formation and utilization play an important role from the very inception of germination. The growth initiation process in the germinating embryo can be explained in the following manner :

Ascorbic acid which is synthesized from sucrose and other sugars helps in the faster uptake of water. It also activates the enzymic systems which are responsible for the mobilization of reserve substances, giving rise to sucrose and other soluble products like aminoacids and fatty acids. Auxins are liberated from the bound state and they catalyze the synthesis of ascorbic acid as well as the enzyme systems acting upon it. As the chlorophyll is synthesized in the seedling further production of ascorbic acid takes place and at the same time its utilization increases. Due to rising

concentration of this powerful agent of the redox system, the reductive atmosphere is created in the plant although its utilization is increased. Ascorbic acid acts as an electron donor in photosynthetic as well as oxidative phosphorylation with which the formation of ATP is coupled. It creates a favourable redox balance for the synthesis of nucleic acids, proteins, enzyme proteins and cell wall constituents as shown by Chinoy (1962), thus enabling the twin process of cell division and enlargement to proceed at a faster rate.

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EFFECT OF WATER STRESS ON CATALASE ACTIVITY OF WHEAT SEEDLINGS

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Abstract

Effects of different periods of desiccation treatments on catalase activity of pretreated and untreated seedlings of wheat N.P. 710 were studied during germination.

The enzymic activity was higher in the embryo compared to that in the endosperm.

Pretreatment with 25 mg / l ascorbic acid solution was beneficial for catalase activity. The enzymic activity increased with advance of growth. On the other hand catalase activity decreased in seedlings subjected to desiccation treatment while in revived seedlings it increased considerably. This suggests that shift in the redox balance of the system is to the oxidative side.

Introduction

Drought resistance of plants depends on the degree of dehydration which their protoplast can endure. Hence it becomes necessary to investigate the relationship of drought resistance with the biochemical and physiological aspects of protoplasm.

Presowing hardening treatment has been reported to increase considerably the drought resistance of plants (Henckel, 1961). The beneficial effect of pretreatment of seeds with growth regulators and other substances has also been reported by other workers (Gupta, 1956; Nanda et al., 1959; Denisova, 1962; May et al., 1962; Salim and Todd, 1968). Presowing treatment leads to an increase in tissue hydration, respiratory activity, redistribution of nutrient reserves and enhancement of seedling growth (Henckel, 1961; Dawson, 1965). Pretreatment with ascorbic acid

accelerated germination processes as well as growth and yield of mature plants (Chinoy, 1967). Chinoy (1968) has shown the importance of presowing treatment of seeds for inducing resistance to drought and salinity in crop production.

The present paper deals with the effect of different periods of desiccation on the enzymic activities of pretreated and untreated seeds of wheat during germination.

Material and Method

Seeds of *Triticum aestivum* L. var. N.P. 710 were given the following pretreatments : (*i*) glass, distilled water (DW), and (*ii*) ascorbic acid solution 25 mg./1 (AA). The method of pretreatment and desiccation treatment has been described elsewhere.*

The enzymic activity was studied in the seedlings thus treated at different growth stages. The estimations were carried out separately in the embryo and endosperm up to the 8th stage of germination (Fig. 1). Three estimations were carried out : (*i*) before the initiation of the desiccation treatment i.e. in the undesiccated material (*ii*) at the end of the desiccation period and (*iii*) after revival. Thus there were in all 360 treatment combinations in this complex experiment comprising of different combinations of 3 pretreatments ×5 desiccation treatments ×8 seedling growth stages and 3 replicates.

Catalase activity was determined by the method of Chance and Maehly (1955) and expressed as an O_2 evolved/min./g.dry.wt.

Results

Considering the complex nature of the experiments the results are grouped to bring out the effects of single factors as well as those of interactions. Thus, for instance, to determine the effect of pretreatments the values for 120 treatment combinations of 5 desiccation treatments, 8 seedling growth stages and 3 replicates are added up and divided by the number of determinations (120) to obtain mean values for the three treatments. Similarly values given in histograms for eight seedling growth stages

*Paper on *Ascorbic acid turnover of pretreated seedlings during water stress* is sent for publication to the Annals of Botany Journal.

and five desiccation treatments are mean values of 45 and 72 determinations respectively and so on for the interactions.
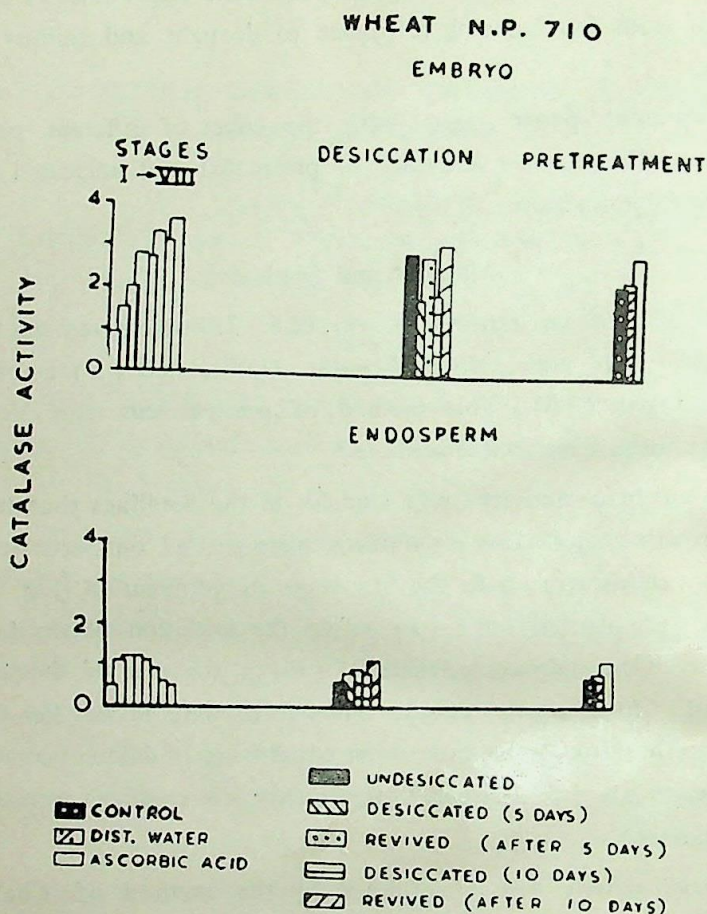
WHEAT N.P. 710

EMBRYO

SINGLE FACTOR EFFECTS

Fig. 1 : Catalase activity in wheat N.P. 710

The following main points emerge from the data :

(1) There is a progressive increase in the catalase activity with the advance in stages of seedling growth in the embryo axis. In case of endosperm there is a continuous fall in catalase activity after the initial rise in the third stage (Fig 1).

(2) There is a sharp fall in catalase activity of the embryo axis during both 5-day as well as 10-day desiccation. In the endosperm on the other hand there is a tendency for enhancement in catalase activity (Fig. 1).

(3) Catalase activity of embryo axis of ascorbic acid pretreated seeds is significantly higher compared with that of the untreated as well as distilled water pretreated embryo axis. AA-pretreatment also accelerates the catalase activity of endosperm.

(4) The highly significant enhancing effect of AA-pretreatment on catalase activity over the other two treatments is again clearly brought out when these data are considered separately for the five desiccation treatments (Fig. 2). This enhancement is highly significant both for the embryo axis as well as the endosperm (Table 1).

WHEAT N.P. 710

EMBRYO

ENDOSPERM

DESICCATION TREATMENTS

CONTROL
DIST. WATER
ASCORBIC ACID
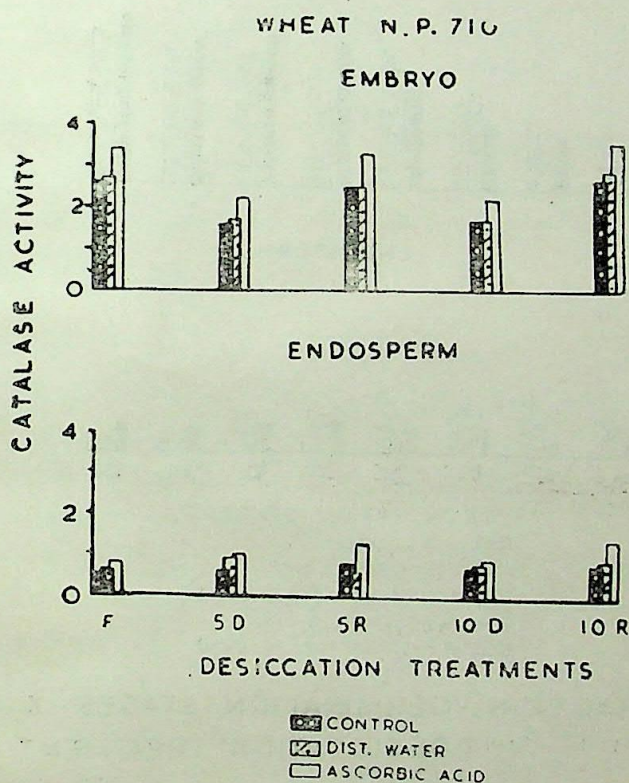
INTERACTION :- PRETREATMENT X DESICCATION TREATMENT

Fig. 2 : Catalase activity in wheat N.P. 710

(5) Studying the results of catalase activity for the five desiccation treatments separately for the eight stages of germination (Fig. 3), it becomes clear that there is a rising trend in the enzymic activity of embryo axis

with advance in germination and fall in the activity of the endosperm. Once again there is a sharp decline in the catalase activity of desiccated embryo axis, which attains almost original levels and sometimes surpasses them during the period of revival. Endosperm also shows similar decline in catalase activity during desiccation with subsequent upserge in the enzymic activity after revival.
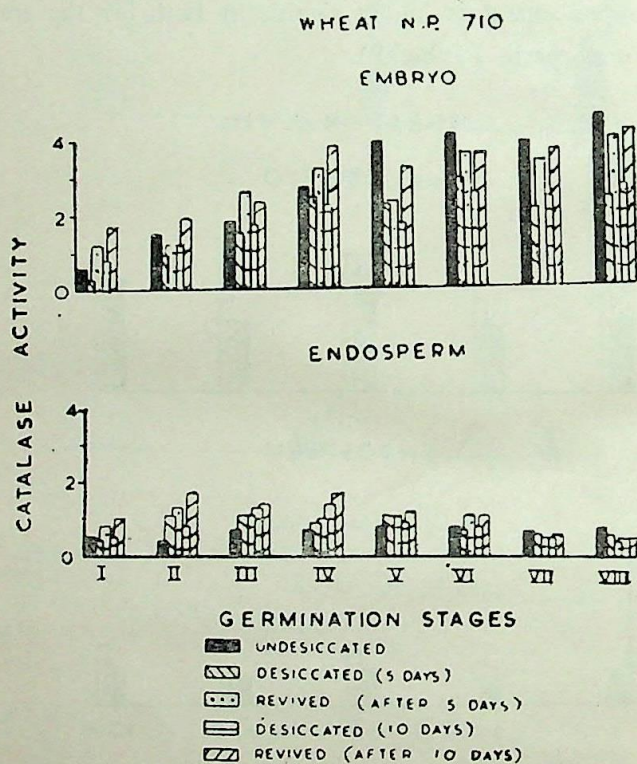
Fig. 3 : Catalase activity in wheat N.P. 710

Statistical significance of the data

The data of catalase activity was subjected to analysis of variance using Fisher's method (1954). The analysis is presented in Table 1.

Effects of desiccation, pretreatment and germination stages were highly significant ($P > 0.01$).

TABLE 1

Analysis of Variance of data of catalase activity in Wheat N.P. 710

Factor	Degree of freedom	Embryoaxis		Endosperm	
		Variance	F value	Variance	F value
Pretreatment	2	17.75	136.5 S	4.71	78.5 S
Desiccation treatment	4	24.84	191.1 S	2.00	33.3 S
Stage	7	39.38	302.9 S	3.78	63.0 S
Replicates	2	2.47	19.0 S	0.93	15.5 S
A × B	8	1.14	8.8 S	0.36	6.0 S
A × C	14	6.13	47.2 S	0.08	1.3
B × C	28	1.76	13.5 S	0.37	6.2 S
Error	294	0.13	—	0.06	—
Total	359	—	—	—	—

S : Denotes significant effect of treatments and their interactions at 1 % P.

Discussion

The results suggest that the major centre of enzymic activity is the embryo and not the endosperm. The enhanced growth activities of pretreated seedlings is presumably due to enhanced catalase activity of pretreated seeds. Treatment with ascorbic acid renders the seedlings drought tolerant. Desiccation treatment increases the concentration of the cell constituents, raises the osmotic value and this brings a number of molecules of different kinds in closer alignment with each other thus promoting more efficient metabolic activity.

The enhanced catalase activity in the germinating seedling with advance of growth, especially in those revived after undergoing desiccation treatment, indicates that the catabolic processes are dominant and the resulting break-down products function as precursors for the biosynthesis of different metabolites.

An enhancement in the oxidative activities as indicated by the increased catalase activity is suggestive of the shift in the redox balance of the system to the oxidative side. The increase in the general metabolism of desiccated seedling caused by the oxidative shift of the redox balance is at the expense

of the breakdown products of essential metabolites and the energy libera-
tion being unproductive. Polimbetova et al., (1964) also expressed similar
view. As the catabolic processes surpass the anabolic processes the growth
of the seedling comes- to a standstill. This is quite evident from the fact
that during the period of desiccation no further growth of the seedling is
observed, i.e., during 5 and 10 days of desiccation the seedling remains
at the same stage at which it was desiccated.

Jaikaria (1971) observed that in *Cicer* seedlings, the enhanced cata-
lase activity parallels with greater utilization of ascorbic acid during desicca-
tion, suggesting that the faster production of H_2O_2 during faster ascorbic
acid utilization is used as a substrate by increased catalase and peroxidase
activities, thereby affording protection to the plant against peroxidative
damage.

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RELATION BETWEEN POLARITY OF ALCOHOLS AS SOLVENT AND hR$_f$ VALUES OF AMINO ACIDS AS SOLUTE BY TLC

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The amino acids in their zwitterionic forms are considered very polar substances, and their separation by thin layer chromatography had been done using many solvent systems.[1-4] The satisfactory separation can often be accomplished using polar alcohol such as methanol, ethanol, n-propanol as components but have major drawback that they give relatively diffuse spots and tend to cause tailing, which may be removed or checked by adding few volume per cent of dilute acetic acid.

In view of this, by thin layer chromatography using silica gel *G* as a polar adsorbent and amino acids as solutes, we have tried n-butanol, n-amyl alcohol, n-hexanol and cyclohexanol as one of the components in solvent system of alcohol + acetic acid + water. The volume of acetic acid and water were kept constant, while the volume of alcohol was taken in such an amount that the gram mole of hydroxyl functional group remains the same in all the four systems. Thus the solvent systems studied were;

(*A*) n-Butanol + acetic acid + water 53 + 30 + 20 (v/v).
(*B*) n-Amyl alcohol + acetic acid + water 62 + 30 + 20 (v/v).
(*C*) n-Hexanol + acetic acid + water 71 + 30 + 20 (v/v).
(*D*) Cyclohexanol + acetic acid + water 60 + 30 + 20 (v/v).

Experimental

Systems and Reagents
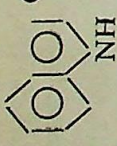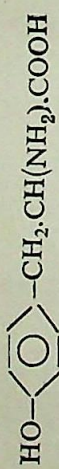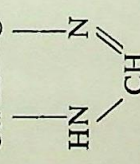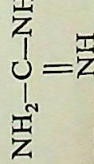
Solution of L-configurated optically active amino acids were prepared by dissolving 5 mgs in 5 ml. 10 % n-propanol. TLC plates were prepared by spreading a mixture of Silica Gel *G* (according to Stahl for TLC, E.

hR$_f$ Values of Some Amino-acids in Solvents A, B, C and D

hR_f Values of Some Amino-acids in Solvents A, B, C and D

No.	Amino acids	Structure	n-Butanol+ Acetic acid +water 53:30:20 (A)	n-Amyl alcohol+ Acetic acid +water 62:30:20 (B)	n-Hexanol+ Acetic acid +water 71:30:20 (C)	Cyclo-hexanol+ Acetic acid +water 60:30:20 (D)
1	2	3	4	5	6	7
(a)	Neutral amino acids :					
1.	Glycine	$NH_2.CH_2.COOH$	48	29	16	40
2.	Alanine	$CH_3.CH(NH_2).COOH$	51	30	20	42
3.	Valine	$(CH_3)_2CH.CH(NH_2).COOH$	58	42	29	47
4.	Norvaline	$CH_3(CH_2)_2.CH(NH_2).COOH$	61	45	33	53
5.	Proline	$NH.CH_2.CH_2.CH_2.CH.COOH$	32	22	13	24
6.	Isoleucine	$CH_3.CH_2.CH(CH_3).CH(NH_2).COOH$	63	53	36	53
7.	Leucine	$(CH_3)_2CH.CH_2.CH(NH_2).COOH$	67	55	40	56
8.	Norleucine	$CH_3(CH_2)_3.CH(NH_2).COOH$	68	55	46	57
(b)	Neutral amino acids containing hydroxyl group :					
9.	Hydroxy-proline	$NH.CH_2.CH(OH).CH_2.CH.COOH$	32	17	07	24
10.	Serine	$HO.CH_2.CH(NH_2).COOH$	41	20	08	33
11.	Threonine	$CH_3.CH(OH).CH(NH_2).COOH$	46	23	10	37
(c)	Neutral amino acids containing aromatic ring :					
12.	Phenyl alanine	$C_6H_5.CH_2.CH(NH_2).COOH$	60	46	31	53

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13. Tryptophan	[structure] CH$_2$.CH(NH$_2$).COOH	64	51	33	55
14. Tyrosine	HO–[ring]–CH$_2$.CH(NH$_2$).COOH	68	53	42	57

(d) Neutral amino acids containing sulphur :

15. Cysteine	HS.CH$_2$.CH(NH$_2$).COOH	23	07	02	13
16. Cystine	[–S.CH$_2$.CH(NH$_2$).COOH]$_2$	27	08	03	15
17. Taurine	NH$_2$.CH$_2$.CH$_2$.SO$_2$OH	40	16	05	24
18. Methionine	CH$_3$SCH$_2$.CH$_2$.CH(NH$_2$).COOH	59	43	29	48

(e) Acidic amino acids :

19. Asparagine	NH$_2$.OC.CH$_2$.CH(NH$_2$).COOH	34	23	11	27
20. Glutamine	NH$_2$.OC.CH$_2$.CH$_2$.CH(NH$_2$).COOH	37	26	13	30
21. Aspartic acid	HOOC.CH$_2$.CH(NH$_2$).COOH	39	28	14	30
22. Glutamic acid	HOOC.CH$_2$.CH$_2$.CH(NH$_2$).COOH	50	35	19	42

(f) Basic amino acids :

23. Lysine	NH$_2$(CH$_2$)$_4$.CH(NH$_2$)COOH	20	10	03	11
24. Ornithine	NH$_2$(CH$_2$)$_3$.CH(NH$_2$).COOH	21	13	04	15
25. Histidine	[structure]	25	13	05	16

26. Arginine	NH$_2$–C–NH.(CH$_2$)$_3$.CH(NH$_2$).COOH, =NH	26	16	05	17

Merck) and distilled water, activated, five microliter spots were applied and
kept in TLC tanks containing solvent systems Nos. A, B, C and D and
0.1 gm. of ninhydrin. When the solvent front reached a height of 10 cm.,
the plates were removed, dried and kept in an oven at 110° C for few
minutes when the spots were detected. The hR_f value was calculated for
all the amino acids. The experimental procedure was carried out at 25° C.

Results

The hR_f values presented in Table I are an average of various
determinations carried out at 25° C.

Discussion

The dielectric constant of n-butanol, n-amyl alcohol, n-hexanol and
cyclohexanol at 25° C are 17.1, 13.9, 13.3 and 15.0. Hence, dielectric
constant of four solvent systems are increasing from n-hexanol to n-amly
alcohol to cyclohexanol to n-butanol. Examining the hR_f values in Table I,
it was observed that for an individual amino acid the hR_f value increases
with increase in the dielectric constant of the solvent system. It is, therefore,
concluded that as the polarity of the alcohol increases the hR_f
value increases.

In neutral amino acids, with the increase in molecular weight the
hR_f value increases, while in isomeric amino acids with the same molecular
weight, n-alkyl amino acid has higher hR_f than iso-alkyl amino acid. With
the introduction of carboxyl, amino or alcoholic group in neutral amino
acids the hR_f value decreases.

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Cu²⁺ and Ni²⁺ CHELATES OF THE OXIME AND THE SCHIFF BASE OF THE KETONE 2-OH-3-Br-5-Me-PROPIOPHENONE

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Abstract

The ligands (*i*) 2-OH-3-Br-5-Me-propiophenonoxime (HL) and (*ii*) 2-OH-3-Br-5-Me propiophenone-ethylene diamine (Schiff base), H_2L' are used here to study their complex-forming behaviour with Cu^{2+} and Ni^{2+}. It is found by analytical, magnetic, conductivity and spectral data that the metal ions give 1:2 complexes with the oxime and can be represented as CuL_2 and NiL_2 and give 1:1 complexes with the Schiff base and can be represented as CuL' and NiL'. All the four complexes are assigned a square planar structure.

Much research work is being done on the analytical and structural aspects of metal complexes of oximes[1] and Schiff bases.[2] It was decided to study the complexes of Cu^{2+} and Ni^{2+} with the 2-OH-3-Br-5-Me-propiophenonoxime, and with the Schiff base formed by condensing 2-OH-3-Br-5-Me-propiophenone with ethylene diamine. Cu^{2+} and Ni^{2+} complexes with the unbrominated ligand 2-OH, 5-Me propiophenonoxime[3] as well as the corresponding unbrominated Schiff base were recently[3] shown to be square planar.

Experimental

(a) Preparation of Oxime

The ketone, 2-OH-3-Me-propiophenone was obtained by Fries migration of p-cresyl propionate[4]. It was next brominated in acetic acid solution. The bromo-ketone was then converted into its oxime (HL) by refluxing for two hours with hydroxylamine hydrochloride[5] in alcohol. The pinkish-white oxime was recrystallised from absolute alcohol. Its m.pt. was 146°C.

(ii) Preparation of Schiff base :

The Schiff base 2-OH-3-Br-5-Me-propiophenone-ethylene diamine (H_2L') was prepared by condensing 2 moles of bromoketone (2-OH-3-Br-5-Me-propiophenone) with one mole of ethylene diamine in presence of absolute alcohol by refluxing the mixture for two hours. The yellow Schiff base formed was recrystallised from chloroform when it showed a m.pt. of 256°C.

(iii) Preparation of Metal chelates :

(a) Chelates with Oxime :

The metal sulphates (Analar $CuSO_4$, $5H_2O$ and $NiSC_4$, $6H_2O$) were refluxed with the oxime ligand in an acetate buffer of pH=6 to 7 for two hours. The precipitated chelates were washed with water to remove the excess of metal salts and finally recrystallised from chloroform. The colour of the copper chelate is ashlike and that of the nickel one is greenish. The chelates are insoluble in water, sparingly soluble in alcohol but soluble in chloroform, acetone, benzene, etc. They are stable in air upto a temperature of 150° C.

(b) Chelates with Schiff base

The metal chelates of Schiff base were prepared by refluxing an excess of the corresponding metal salts and Schiff base (H_2L') for about one hour in alcohol with constant stirring, The solid chelates were filtered and washed with water to remove an excess of metal salt and finally recrystallised from chloroform. The copper chelate is dark green and the nickel one is bright yellow. They are insoluble in water, less soluble in alcohol and soluble in chloroform, benzene, acetone, etc. They are stable in air upto a temperature 150° C.

(*iv*) Analysis of chelates : Oxime chelates and Schiff base chelates

The chelates were broken by a small quantity of sulfuric acid. The percentage of metal in each case was estimated by standard analytical methods. Bromine in each case was estimated by Kay–and Haywood[6] method. The percentage of the metal and bromine showed that the complexes were 1:2 in composition in the case of oxime chelates and 1:1 in the case of the Schiff base. The mol. wts. determined cryoscopically using camphor as a solvent, showed the chelates to be monomeric i.e, the chelates could be represented as ML_2 in the case of oxime chelates, and ML^1 in the case of Schiff chelates. The details of the analysis are given in Table 1. Their conductivity in chloroform solution was very low proving the non–electrolytic[8] nature of the oxime and the Schiff base chelates. The oxime chelates and Schiff base chelates therefore, are given the following structure :

(*a*) Oxime chelates :

(*b*) Schiff base chelates :

$$M^{2+} = Cu^{2+} \; or \; Ni^{2+}$$
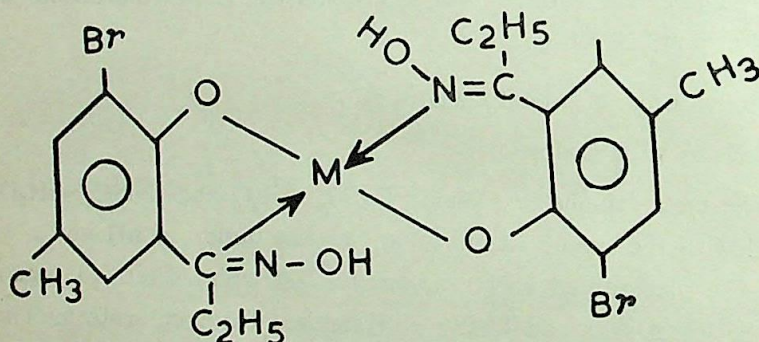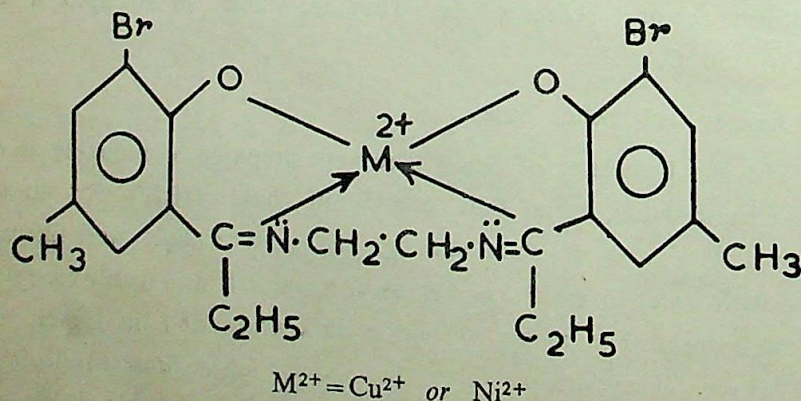
TABLE I

Sr. No.	Complexes	Metal estimation		Br estimation		Mol. wts.		Molar Conductance (mhos cm² mole⁻¹)
		Found %	Expected %	Found %	Expected %	Found	Expected	
A	**Oxime Complexes**							
(i)	CuL_2	11.134 %	10.992 %	28.04 %	27.7 %	566.8 572.5	577.54	5
(ii)	NiL_2	10.935 %	10.940 %	27.91 %	28.21 %	568.2 574.4	572.71	5
B	**Schiff Complexes**							
(i)	CuL'	10.992%	11.02 %	28.43%	28.0 %	566.8 574.2	571.54	5
(ii)	NiL'	10.355 %	10.325 %	28.72 %	28.24%	568.2 568.2	566.71	5

(*v*) Magnetic properties

The two copper complexes have a magnetic moment of 1.89 B.M. (oxime) and 1.86 B.M. (Schiff). These are not much different from the spin-only value of 1.73 B.M. for one unpaired electron. Hence it is concluded that these copper complexes contain one unpaired electron which is as expected[7,8]. It is presumed that the copper complexes are square planar in structure[7,8]. Both the Ni^{2+} complexes are diamagnetic, suggesting a square planar[7,8] structure with $^1A_{1g}$ ($eg^4 b_{2g}^2 a_{1g}^2$) as the ground state.

(*vi*) The electronic spectra

The absorption spectra of these four compounds, listed in Table II, can be co-related with the structures assigned to them.

<div align="center">

TABLE II

Absorption Spectra and Magnetic characteristics
</div>

Sr. No.	*Chelates*	*Maxima (nm)*		χ_M *Corr* $x\ 10^6$ *c.g.s.*	μeff *(B.M.)* *at* 37°C
A Oxime chelate					
1.	CuL_2	620	60		
		480	105	1436	1.892
		390	2800		
2.	NiL_2	610	42		
		460	100	−78.3	0.0
		390	1600		
B Schiff base chelates					
1.	CuL'	620	120		
		540	230	1389	1.861
		410	7200		
2.	NiL'	490	325		
		425	2560	−74.4	0.0

Oxime Complexes :

CuL_2 : The band[9,10] at 620 nm ($\varepsilon = 60$) could be $^2A_{1g} \leftarrow {}^2B_{1g}$ and the one at 480 nm ($\varepsilon = 105$) could be $^2E_g \leftarrow {}^2B_{1g}$. The band at 390 nm could be a charge transfer (C.T.) band.

NiL_2 : The band[11,12] at 610 nm ($\varepsilon = 42$) could be $^1B_{1g} \leftarrow {}^1A_{1g}$ and the other at 460 nm (100) could be $^1E_g \leftarrow {}^1A_{1g}$. The band at 390 nm could be a C.T. band.

Schiff base complexes

CuL : The bands at 620 nm and at 540 nm could have an origin[9],[10] similar to the corrosponding oxime–chelates at 620 nm and 480 nm. The band at 410 nm could be a C. T. band.

NiL : The band[11],[12] at 490 nm could be $^1B_{1g} \leftarrow {}^1A_{1g}$ while the other at 425 nm might be a C. T. band.

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CORROSION OF 3S AND B26S ALUMINIUM BY AQUEOUS SOLUTIONS OF SOME ACIDS*

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Abstract

Corrosion of aluminium (3S) and Al–Cu (4%) alloy (B26S) in solutions of different acids has been studied with respect to the time of immersion and concentration of the acid. The corrosivity of the acids is in the order : Trichloroacetic $>$ hydrochloric $>$ orthophosphoric $>$ nitric $>$ sulphuric $>$ oxalic $>$ monochloroacetic $>$ formic $>$ acetic $>$ succinic $>$ benzoic acid. In general B26S alloy corrodes to a greater extent than 3S aluminium. The high rate of corrosion in trichloroacetic acid may be attributed to its reduction to hydrochloric acid by an autocatalytic cycle.

Aluminium and its alloys are preferred as materials of construction in many fields because of their lightness and ability to resist corrosion. In everyday applications the pure metal is not much used but an intimate blend of aluminium and other elements. Although thermodynamically aluminium reacts with oxygen spontaneously to give aluminium oxide according to the reaction[1],

$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 800 \text{ K.cal} \qquad \ldots (1)$$
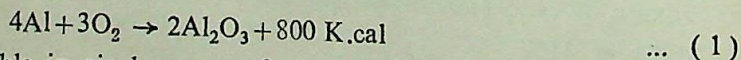
the metal is stable in air because of the presence of an exteremly thin but remarkably tight and adherent, invisible oxide film on the metal surface. As a general rule, the protective oxide film is stable in aqueous solutions

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in the pH range of 4.5 to 8.5 but is readily soluble in strongly acid or alkaline solutions.[2] However, the corrosivity of an environment cannot be determined only by its pH, because the nature of the individual ions in the solution may be the controlling factor.

Although corrosion of aluminium in acid solutions has been studied by a number of workers, the comparative information about corrosion of aluminium, especially Al–Cu alloy, in different acids is not much available [3, 4, 5, 6]. In earlier communications [7, 8, 9, 10, 11] the corrosion of aluminium in aqueous solutions of some acids has been reported. In the present investigation the corrosion of 3S (1.2% Mg) and B 26 S (4 % Cu) aluminium in aqueous solutions of some acids has been studied with respect to the time of immersion and concentration of the acid.

Experimental Procedure :

The metal samples (supplied by Indian Aluminium Co. Ltd., Bombay) used in the investigation had the following composition :

3S   Aluminium :   Cu—0.15; Fe—0.70; Si—0.60;
                              Mn—1.0—1.5; Zn—0.10;
                              Al—remainder.

B26S   Aluminium :   Cu—3.8—4.8; Fe—0.7;
                              Si—0.5—0.9; Mn—0.3—1.02;
                              Mg 0.2—0.8, Al—remainder.

The specimens (5×4 cm) were polished according to the method described earlier[12, 13] using tripoli composition. One specimen was suspended in each beaker containing 230 ml of the acid solution and left exposed to the air at 30±0.5 °C. The specimens were cleaned after the tests with chromic-phosphoric acid mixture.[14]

Results and discussion :

The results are presented in tables 1 and 2. The specimens immersed in solutions of benzoic acid remained as bright as before whereas those immersed in solutions of succinic, acetic, monochloroacetic, formic, oxalic and sulphuric acid and in dilute solutions of other acids developed a film of grayish, loose product which could be easily removed with a jet of water or by rubbing with a rubber bung. The film material when separated

TABLE 1

Effect of acid concentration and immersion period on the corrosion (mg/dm^2) of B26S aluminium

(Surface area of the specimen, 40 sq. cm., temp. 30°C)

		1 Day				3 Days				5 Days			
Acid	Acid conc(N): pKa	0.01	0.05	0.1	1.0	0.01	0.05	0.1	1.0	0.01	0.05	0.1	1.0
(1) Benzoic	4.201[17]	*	*	—	—	*	*	—	—	*	1	—	—
(2) Succinic	4.207[17]	*	*	1	2.5	1.2	5	6.5	7.5	2.5	6	7.5	8.5
(3) Acetic	4.756[17]	*	1	2.5	5	2.5	3.7	7.5	19	5	17.5	19	26
(4) Monochloroacetic	2.861[17]	3.5	7.5	9	15	9.5	12.5	15.5	25	11.2	17.5	27.5	35.5
(5) Formic	3.752[17]	*	1	6	7.5	3.7	8.5	17.5	28.2	17.5	25	33.5	47.5
(6) Oxalic	1.271[17]	18.5	23	25	27.5	42.5	47.5	65	90	52.5	120	142	157.5
(7) Sulphuric	1.92[17]	27.5	32	35	67.5	52.5	89.5	101	177.5	62.5	137.5	157	380
(8) Nitric	—	13.5	26	47.5	162.5	40	110	154	447.5	50	174	251	475
(9) Orthophosphoric	2.148[17]	12.5	26.2	91.2	282.5	17.5	62.5	270	830	25	107.5	350	1350
(10) Hydrochloric	0.04[19]	15	21	30	6225	38	67.5	84	8875	47	119	152.5	9225
(11) Trichloroacetic	0.89[18]	27.5	807.5	2157.5	D	497.5	1326	3415	D	946	3209	3947	D

* Indicates almost no corrosion

D indicates almost complete dissolution of the specimen.

TABLE 2

Effect of acid concentration and immersion period on the corrosion (mg/dm^2) of 3S aluminium

(Surface area of the specimen., 40 sq. cm., temp. 30°C)

| Acid / Acid concentration:	1 Day				3 Days				5 Days			
	0.01	0.05	0.1	1.0	0.01	0.05	0.1	1.0	0.01	0.05	0.1	1.0
(1) Benzoic	*	*	—	—	*	3	—	—	*	3	—	1.0
(2) Succinic	*	*	*	1.5	*	*	6.2	9	14	10	18.5	21.5
(3) Acetic	*	*	*	2.5	*	2.5	4.5	12.5	3.7	7.5	12.5	25
(4) Monochloroacetic	*	2.5	8.7	15.7	10	23.2	28.7	42.5	17.5	31.2	50	67.7
(5) Formic	*	*	7.5	15	2.5	13.7	17.5	36.2	7.5	28.7	41.2	69
(6) Oxalic	1.2	2.5	8.7	23.75	37.5	118.7	127.5	175	50	127	147	200
(7) Sulphuric	32.5	42.5	50	75	61.5	115	133.7	238.5	67.5	168.7	224.7	395
(8) Nitric	23.7	35	42	103.7	40	92.5	105	555	47.5	137.5	185	627.5
(9) Orthophosphoric	16.2	47.5	85	300	21.2	71.7	285	900	30	110	425.5	1367
(10) Hydrochloric	25	35	47.5	4912.5	51.7	87.5	107.5	4980	57.7	138.7	470	6120
(11) Trichloroacetic	27.5	807.5	2162	D	498.5	1326.7	3496	D	846.7	3254	3967	D

* Indicates almost no corrosion

D indicates almost complete dissolution of the specimen.

from the specimen by rubbing, dissolved in the acid and thus appeared to be due to the presence of cathodic elements. The cleaned specimens had a slightly dull metallic appearance. In concentrated solutions of nitric, o-phosphoric, hydrochloric and trichloroacetic acids there was very little film formation and the extent of corrosion and the number as well as the size of the pits increased with time. Later on the corrosion was so intense that there was grooving and chanelling all over the surface, showing the direction of hydrogen evolution. In concentrated solutions, the specimens were at times perforated and fell down from the glass hooks. In the case of B26S alloy, a reddish product settled down at the bottom of the beaker.

Aqueous solutions of benzoic, succinic and acetic acid and very dilute solutions of monochloro and formic acid are much less corrosive, the extent of corrosion being about 1 to 26 mg/dm^2; those of monochloro-acetic acid and oxalic acid are moderately corrosive while trichloroacetic and concentrated solutions of sulphuric, nitric, o-phosphoric and hydrochloric acids are very highly corrosive (corrosion loss more than 150 mg/dm^2). This agrees with a report [3,4] that most of the organic acids are well resisted by aluminium alloys at room temperature. In all the acids the extent of corrosion increased with increase in the concentration of acid and the time of immersion. On the whole B 26 S alloy corroded to a greater extent than the 3S aluminium, this being more so in highly corrosive solutions. The high rate of corrosion of B 26 S alloy may be attributed to the fact that copper can act as an efficient metallic cathode relative to the other metals in acid solutions.[15] For dilute solutions the lower values of corrosion loss may be traced to the fact that aluminium tries to develop an oxide film on the metal surface provided the hydrogen ion concentration is low, sufficient oxygen is available and there are no film penetrating anious present in the solution.

Generally aluminium dissolves in acid solutions due to hydrogen evolution type of attack, the reactions taking place at the microelectrode of the corrosion cell being represented as

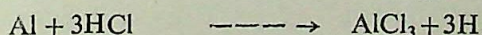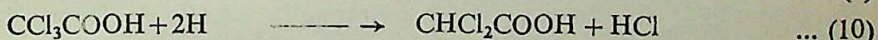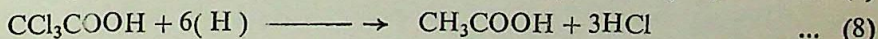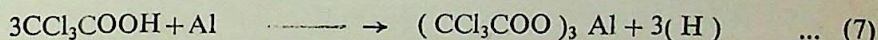$$Al \longrightarrow Al^{3+} + 3e \ldots\ldots anode \qquad \ldots (2)$$

$$H^+ + e \longrightarrow H \ (ads) \ldots\ldots cathode \qquad \ldots (3)$$
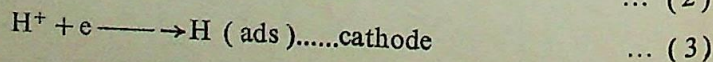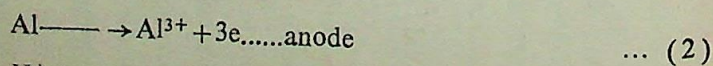
followed by the reaction

$$H + H \cdot \longrightarrow H_2(g)......\qquad\qquad ... (4)$$

The following secondary reactions can also take place in acid solutions[16]

$$2M + 2H^+ \longrightarrow H_2 + 2M^+......\ (anode)\qquad ... (5)$$

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O......(cathode)\qquad ... (6)$$
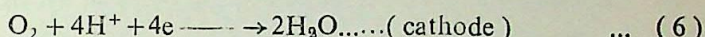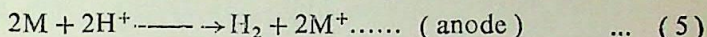
If, therefore, only the hydrogen evolution type of attack is predominant and no other factors influence the corrosion process, corrosion by the strongest acid should be the maximum. On the basis of the dissociation constants, the strength of the acids studied is in the order : acetic > succinic and benzoic > formic acid > monochloroacetic > orthophosphoric > oxalic > sulphuric (K_2) > trichloroacetic acid > nitric > hydrochloric acid. It is apparent from the results given in table I and II that at higher concentrations and for longer periods of immersion, the corrosion increases with increase in the dissociation constant of the acid in the case of many of the acids, the apparent exceptions being oxalic, nitric, sulphuric and trichloroacetic acid. In the case of nitric acid the exception may be traced to the oxidative nature of the acid, whereas in the case of oxalic acid it may be traced to the insolubility of the oxalates.

As already suggested in a previous communication[11], the exceptionally high rate of corrosion in trichloroacetic acid may be attributed to the reduction of trichloroacetic acid into dichloroacetic, monochloroacetic and hydrochloric acids according to the following reactions :

$$3CCl_3COOH + Al \longrightarrow (CCl_3COO)_3\ Al + 3(H)\qquad ... (7)$$

$$CCl_3COOH + 6(H) \longrightarrow CH_3COOH + 3HCl\qquad ... (8)$$

$$CCl_3COOH + 4H \longrightarrow CH_2ClCOOH + 2HCl\qquad ... (9)$$

$$CCl_3COOH + 2H \longrightarrow CHCl_2COOH + HCl\qquad ... (10)$$

$$Al + 3HCl \longrightarrow AlCl_3 + 3H$$

The autocatalytic nature of the cycle and presence of highly penetrating chloride ions, therefore, appear to be particularly responsible for the high corrosivity of the trichloroacetic acid.

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SYNTHESIS OF N⁴-(p-PIPERIDINOSULFONYL-PHENYL) THIOCARBAZONES

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4-Substituted thio semicarbazides have been described in literature very scantily.[1] Several thio semicarbazones show chemotherapeutic activities.[2, 3]

Thio-ureas having sulfonamide moeity are used as antidiabetic compounds, while sulfonamides containing basic acylamido groups show hypoglycemic activity.[4]

We thought of combining thio semicarbazides and phenyl sulphonyl moeity to synthesise compounds which may show some chemo-therapeutic activity. Thus various N⁴-(p-piperidino sulfonylphenyl) thio semicarbazones have been synthesised and described in the present communication (vide Table I).
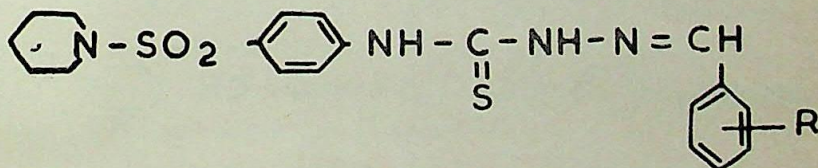
R	Molecular Formula	mp.	% N Found	Cal.
1. H	$C_{19}H_{22}N_4S_2O_2$	216° C	13.74	13.93
2. p-Cl	$C_{19}H_{21}N_4S_2O_2Cl$	227° C	12.68	12.83
3. O-OH	$C_{19}H_{22}N_4S_2O_3$	221° C	13.18	13.39
4. 3, 4, Methylene dioxy	$C_{20}H_{22}N_4S_2O_4$	206° C	12.35	12.55
5. 1-Napthalde-hyde	$C_{23}H_{24}N_4S_2O_4$	211° C	12.49	12.66
6. O-Furfuryl	$C_{17}H_{20}N_4S_3O_3$	174° C	14.12	14.28

p-amino phenylsulfonyl piperidine was converted to p-isothiocyanato phenylsulphonyl piperidine using thiophosgene in chloroform as solvent. Treatment of hydrazine hydrate with this isothiocyanate in ethanol afforded N^4-(p-piperidino sulfonylphenyl) thio semicarbazides.

These condensed with various aldehydes to get the title compounds. These thio semi-carbazones did not show any specific physiological activity.

A reaction of chloroacetic acid with above thio-semicarbazones and subsequent cyclisation afforded thiozolidone derivatives. These products could either be 3-Benzylidine amino-2-(piperidino sulfonyl p-phenyl imino)-4-thiozolidone (Structure 1) or 3 (piperidino sulfonylphenyl)-2- (Benzylidine amino-imino)-4- thiozolidone (Structure 2). These compounds showed a weak anti-bacterial activity. The constitution of these products turned out to be complex in nature and is under study (vide Table II).
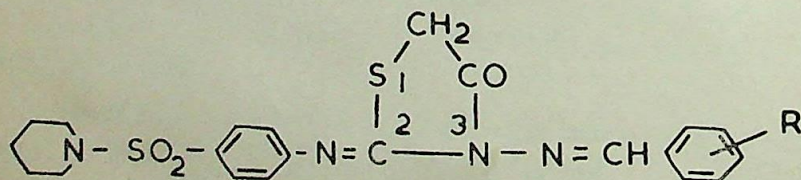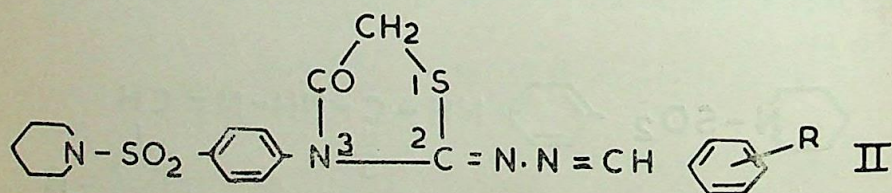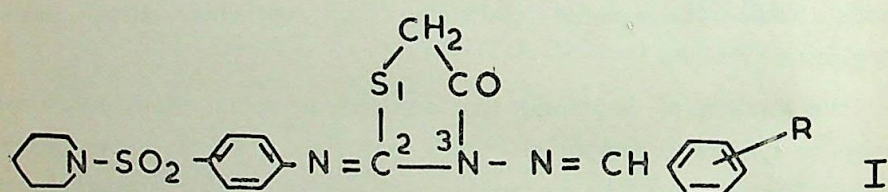
OR

R	Molecular Formula	mp.	%N Found	%N Cal.
1. H.	$C_{21}H_{22}N_4S_2O_3$	187° C	12.46	12.69
2. p-Cl	$C_{21}H_{21}N_4S_2O_3Cl$	144° C	11.53	11.75
3. O-OH	$C_{21}H_{22}N_4S_2O_4$	230° C	12.00	12.27
4. 3, 4, Methylene dioxy	$C_{22}H_{22}N_4S_2O_5$	135° C	11.35	11.52
5 O-Furfuryl	$C_{19}H_{20}N_4S_2O_4$	124° C	12.72	12.96

Experimental

1. p-isothiocyanato phenylsulphonyl piperidine was prepared by thiophosgene method as described in previous communication (P. S. Acharya, J. P. Trivedi, 'Vidya', under publication).

2. Preparation of N^4–(p-piperidino sulfonylphenyl) thio semicarbazones:

    1M of p-isothiocyanato phenylsulfonyl piperidine and 1M of hydrazine hydrate in absolute ethanol refluxed for 2 hours. On cooling crystals separated in quantitative yield mp. 194° C. Recrystallised from ethanol mp. 196° C.

3. Preparation of N^4–(p-piperidino sulfonylphenyl) thio semicarbazides:

    1M of N^4–(p-piperidino sulfonylphenyl) thio semicarbazone and 1M of aromatic aldehydes in benzene and a drop of concentrated HCl was refluxed on water bath for one hour. On cooling the product separated yield nearly quantitative.

4. 3-Benzylidine amino-2-(piperidino sulfonyl-p-phenyl imino)-4-thiozolidone; or

    3-(piperidino sulfonyl-p-phenyl)-2-(Benzylidine amino imino) -4-thiozolidone :

    1 M of N^4–(p-piperidino sulfonylphenyl) thio semicarbazide and 1M of chloroacetic acid in ethanol was refluxed with 1M of fused sodium acetate for five hours on a steam bath. Ethanol was distilled out and product treated with cold water. The solid obtained filtered, washed with water, dried and crystallised from acetic acid yields 45 to 50%.

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Acknowledgement

SYNTHESIS OF SULFONAMIDES AS POSSIBLE HYPOGLYCEMIC AGENTS

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Summary

Sulfonamides are a major class of chemotherapeutic agents. Several variations on the N–1 atom are known to give various chemotherapeutic agents. Substitution on N–4, however, does not show any chemotherapeutic activity.[1,2].

Ureas and thioureas having the sulfonamide moeity are found to be successful antidiabatic compounds e.g. tolbutamide. Recently, Tozaburo and Hido[3] have synthesised several sulfonamides where p–amino groups are substituted by basic acylamido groups. Some of the compounds showed promising hypoglycemic activity.

Keeping this view in mind, it was of interest to prepare several basic amides of sulfanilamide substituted at N–4. Acetanilide was subjected to chlorosulfonylation to obtain p–acetamidobenzenesulfonyl chloride. This was condensed with piperidine and the resulting p–acetamido–phenylsulfonyl piperidine was hydrolysed by H^+ to get p–aminophenylsulfonyl piperidine (A). This served as the basic starting material.

Two major reactions were investigated. A was condensed with chloroacetylchloride or α–bromopropionyl chloride to get the corresponding ∝–halo–p-acetamidophenylsulfonyl piperidine derivatives. These were condensed with various secondary amines to get ω–dialkylaminophenyl-sulfonyl piperidines. The compounds thus synthesised are described in Table 1.

TABLE I

$$\langle \rangle N - SO_2 - \langle \rangle - NH - CO - CH_2 - R$$

R	Molecular Formula	mp	HCl salt	%N Found	%N Cal.
1. Piperidine	$C_{16}H_{27}N_3SO_3$	148°	221°	12.19	12.31
2. Piperazine	$C_{17}H_{38}N_4SO_9$ (HCl)	—	221°	10.79	10.96
3. Morpholine	$C_{17}H_{25}N_3SO_4$	136°		11.32	11.45
4. Diethylamine	$C_{17}H_{27}N_3SO_3$	141°		11.71	11.87

$$\langle \rangle N - SO_2 - \langle \rangle - NH - CO - CH - CH_3$$
$$\underset{R}{|}$$

R	Molecular Formula	mp	HCl salt	%N Found	%N Cal.
1. Piperidine	$C_{19}H_{29}N_3SO_3$	201°		10.94	11.08
2. Piperazine	$C_{18}H_{40}N_4SO_9$ (HCl)		234°	10.52	10.65
3. Morpholine	$C_{18}H_{27}N_3SO_4$	197°		10.89	11.02
4. Diethylamine	$C_{16}H_{29}N_3SO_3$		123°	10.96	11.06

A was treated with thiophosgene in order to get p–isothiocyanato-phenylsulfonyl piperidine. These served as a starting material for the synthesis of p-thioureido phenylsulfonyl piperidine. The compounds synthesised are described in Table II.

The same thioureas were also prepared by condensation of p–amino-phenylsulfonyl piperidine with the corresponding isothiocyanates Additional thioureas thus prepared are described in Table III.

TABLE II

$$\text{N—SO}_2-\langle\ \rangle-\text{NH—C—NHR}$$
$$\overset{\|}{\underset{S}{}}$$

R	Molecular Formula	Melting point	%N Found	%N Cal.
1. Phenyl	$C_{18}H_{21}N_3S_2O_2$	159°	10.98	11.20
2. o–Methoxyphenyl	$C_{19}H_{23}N_3S_2O_3$	171°	10.18	10.37
3. p–Methoxyphenyl	$C_{19}H_{23}N_3S_2O_3$	169°	10.16	10.37
4. o–Methylphenyl	$C_{19}H_{23}N_3S_2O_2$	165°	10.59	10.79
5. m–Methylphenyl	$C_{19}H_{23}N_3S_2O_2$	175°	10.56	10.79
6. p–Methylphenyl	$C_{19}H_{23}N_3S_2O_2$	139°	10.57	10.79
7. p–Chlorophenyl	$C_{18}H_{20}N_3S_2O_2Cl$	89°	10.12	10.25
8. p–Bromophenyl	$C_{18}H_{20}N_3S_2O_2Br$	164°	9.07	9.25
9. Benzyl	$C_{19}H_{22}N_3S_2O_2$	204°	10.64	10.82
10. p–Bromobenzyl	$C_{19}N_{22}N_3S_2O_2Br$	136°	8.89	8.97

TABLE III

$$\text{N—SO}_2\langle\ \rangle-\text{NH—C—NH.R.}$$
$$\overset{\|}{\underset{S}{}}$$
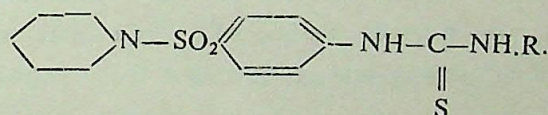
The compounds 1 to 10 are same as those described in Table II.

R	Molecular Formula	mp	% N Found	% N Cal.
11. n–Butyl	$C_{16}H_{25}N_3S_2O_2$	179°	11.70	11.83
12. n–Amyl	$C_{17}H_{27}N_3S_2O_2$	137°	11.25	11.39
13. n–Hexyl	$C_{18}H_{29}N_3S_2O_2$	114°	10.82	10.96
14. Cyclohexyl	$C_{18}H_{27}N_3S_2O_2$	106°	10.89	11.02
15. p–Aminophenyl-sulphonyl	$C_{26}H_{30}N_4S_3O_4$	115°	9.88	10.03
16. Piperidino	$C_{17}H_{25}N_3S_2O_2$	174°	11.33	11.44
17. Diethylamino	$C_{16}H_{25}N_3S_2O_2$	203°	11.70	11.82
18. Morpholino	$C_{16}H_{23}N_8S_2O_3$	153°	11.11	11.25
19. Piperazino	$C_{16}H_{36}N_4S_2O_8$	175°	8.66	8.82

Experimental

1. The compounds p-acetamidobenzenesulfonamide and p-aminobenzene-sulfonamide were prepared by standard procedures as described in Vogel.[4]

2. Synthesis of p-aminophenylsulfonyl piperidine : 1M of piperidine was treated with 1M of p-acetamido–benzenesulfonyl chloride with vigorous stirring and cooling. The mixture was heated for one hour on a water bath and cooled. The product was filtered and washed with water. It was recrystallised from methyl alcohol, mp 171° – 172°.

   p-Acetaminophenylsulfonyl piperidine (10 g) was heated with HCl (50 ml, 15%) on water bath for three hours. The mixture chilled and neutralised with aqueous sodium carbonate to give p-aminophenylsulfonyl piperidine. It was recrystallised from ethyl alcohol, mp 165°; yield 7 g.

3. Synthesis of ∝—halo–p—acetamidophenylsulfonyl–piperidine :

To p-aminophenylsulfonyl piperidine (0.1M) in water (50 ml) cooled in an ice salt mixture was added dropwise with vigorous stirring chloroacetyl chloride or/∝—bromopropionyl chloride (0.11M) and aqueous NaOH (50 ml, 10%) simultaneously, keeping the reaction mixture below 25°. The product obtained was filtered, washed with HCl (1:1) and cold water. The product after air drying was recrystallised from petrol ether. (40-60)

4. Synthesis of ω—dialkylaminophenylsulfonyl piperidine :

To the ∝—halo–p--acetamidophenylsulfonyl chloride (1M) taken in absolute ethanol was added the secondary amine (1M), and the mixture stirred in boiling water bath for six hours. On cooling and leaving it overnight, the title product separated as crystals. It was filtered, dried and recrystallised from petrol ether. In some cases, the semi–solid product separated as a hydrochloride and was recrystallised from petrol ether (Table I).

5. Synthesis of p–isothiocyanato-phenylsulfonyl piperidine :

To a stirring mixture of (0.05M) p-aminophenylsulfonyl piperidine in chloroform (50–100 ml) was added dropwise over 30 minutes this phosgene (0.055M) taken in water (50–100 ml) After the addition of thiophosgene was complete. an aqueous solution of sodium bicarbonate was added and the mixture stirred for 30 minutes more. The reactions mixture was taken

up in ether and dried over anhydrous $MgSO_4$. On removal of ether, the isothiocyanate separated as a solid, mp 125°. Recrystallised from benzene.

6. Synthesis of 4–p–(thio–ureido) phenylsulfonyl piperidine :

To a (1M) of p–isothiocyanate phenylsulfonyl piperidine was added 1M of primary amine in absolute alcohol. The mixture was brought to boiling and left to cool. In about two hours the thiourea separated. It was recrystallised from alcohol (Table II).

The title compounds were also prepared by condensing p–aminophenylsulfonyl piperidine with aryl isothiocyanate in boiling alcohol for two hours. The product recrystallised from alcohol (Table III).

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Acknowledgement

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*If the amino mitrogen (N^4) is substituted by a group that cannot be removed in the body, activity is entirely lost.

HETEROCYCLIC AMINES AS CORROSION INHIBITORS FOR 63/37 BRASS IN POTASSIUM PERSULPHATE SOLUTION

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Potassium persulphate is found highly corrosive to copper and its alloys (1-5). Due to its corrosive characteristics the investigation for suitable inhibitors is essential. In the present work, an attempt has been made to evaluate the inhibitory action of heterocyclic amines (Pyridine, Quinoline and α-Picoline) towards α-type brass in 0.1M potassium persulphate soluti·n.

Experimental

(*i*) Materials : Rectangular specimen (3×6 cms ; 26 S.W.G.) of 63/37 brass was used which had following type of composition :

Cu—63.2%, Zn—36.6%, Sn—0.07% a·d Pb—0.01%

(*ii*) Chemicals : Potassium persulphate of S. Merk was used and 0.1M solution was prepared in distilled water; inhibitors were used of BDH and Riedel.

(*iii*) Procedure : The preparation, testing and cleaning procedures for specimen were adopted as those described in the previous publication[6] 250ml of 0.1M potassium persulphate solution was taken for immersion of each specimen.

Results of weight loss are given in Table 1.

Table 1

Inhibition of corrosion of 63/37 Brass in 0.1N potassium persulphate by heterocyclic amines.

Size of specimen : 3×6 cm.
Duration : 60 minutes
Temperature : $33 \pm 1°$ C.

Concentration of inhibitor (ml/lit.)	Loss mg.	Inhibition (%)	Loss mg.	Inhibition (%)	Loss mg	Inhibition (%)
0.0	370	—	370	—	370	—
	Pyridine		Quinoline		α-Picoline	
2.0	330	11	230	40	240	35
4.0	320	14	205	44	180	51
8.0	98.4	73	198	46	17.0	95
12.0	35.4	90	150	59	11.0	97

Corrosion rate

Potassium persulphate solutions are highly corrosive to metals and alloys, the rate of dissolution being of the order 72 $g/m^2/day$ (1). Sheppard (2) observed that if a strip of brass is dipped completely in potassium persulphate solution, it is blackened immediately, however, if the strip is slowly lowered in $K_2S_2O_8$ solution, either blackening does not occur or a patchy black tarnish is observed on the brass surface. Potassium persulphate can be used to remove oxide layers but is highly corrosive.

In 0 1M potassium persulphate solution decuprification takes plate. Colour of the solution turned bluish green and plate remain dull yellow. In 0.1M potassium persulphate solution 370 mg weight loss was observed at 60 minutes duration at 36°C.

Inhibitor efficiency

Pyridine is found as a poor corrosion inhibitor particularly at its lower concentration. However, It efforded 90% protection at its highest concentration.

In the case of quinoline, plate was covered with thick film which was easily removed in 5% sulphuric acid. It afforded 59% protection at its highest concentration. It is found less effective in inhibitive power than pyridine and α-picoline.

α-picoline afforded maximum inhibition towards 63/37 brass in 0.1M potassium persulphate solution. Its inhibitive power increases with increase in concentration of the compound.

Quinoline is less effective inhibitor. The inhibitive power of quinoline may depend upon the solubility of the complex formed on the metal surface.

Discussion

Heterocyclic amines have been studied as corrosion inhibitors. They have tendency to form brown coloured film on the metal surface. It is qualitatively observed that these compounds give different types of coloured precipitates with copper and zinc ions inpotassium persulphate solution.

Compound	Copper ions	Zinc ions
Pyridine	Bright blue	Wite ppt.
Quinoline	Dark red solution	No ppt.
α-picoline	Dull blue	White ppt.

This is a strong evidance that most of the compounds have tendency to form complex compounds with copper ions and/or zinc ions. Due to the formation of insoluble film α-picoline and pyridine afforded good inhibition.

A rational statement of the problem of the correlation between molecular structure and inhibition has been made by Hackerman (7-8) who developed a theory of adsorption. He concluded that the greater the percentage of π orbitals of the free electrons on the nitrogen atom, the more effective is the inhibitive action.

In the case of α-picoline CH_3 group is attached at 2-position of the pyridine ring,—CH_3 group is electron releasing group. Hence tbe electron density on nitrogen atom increasing, resulting in high inhibition.

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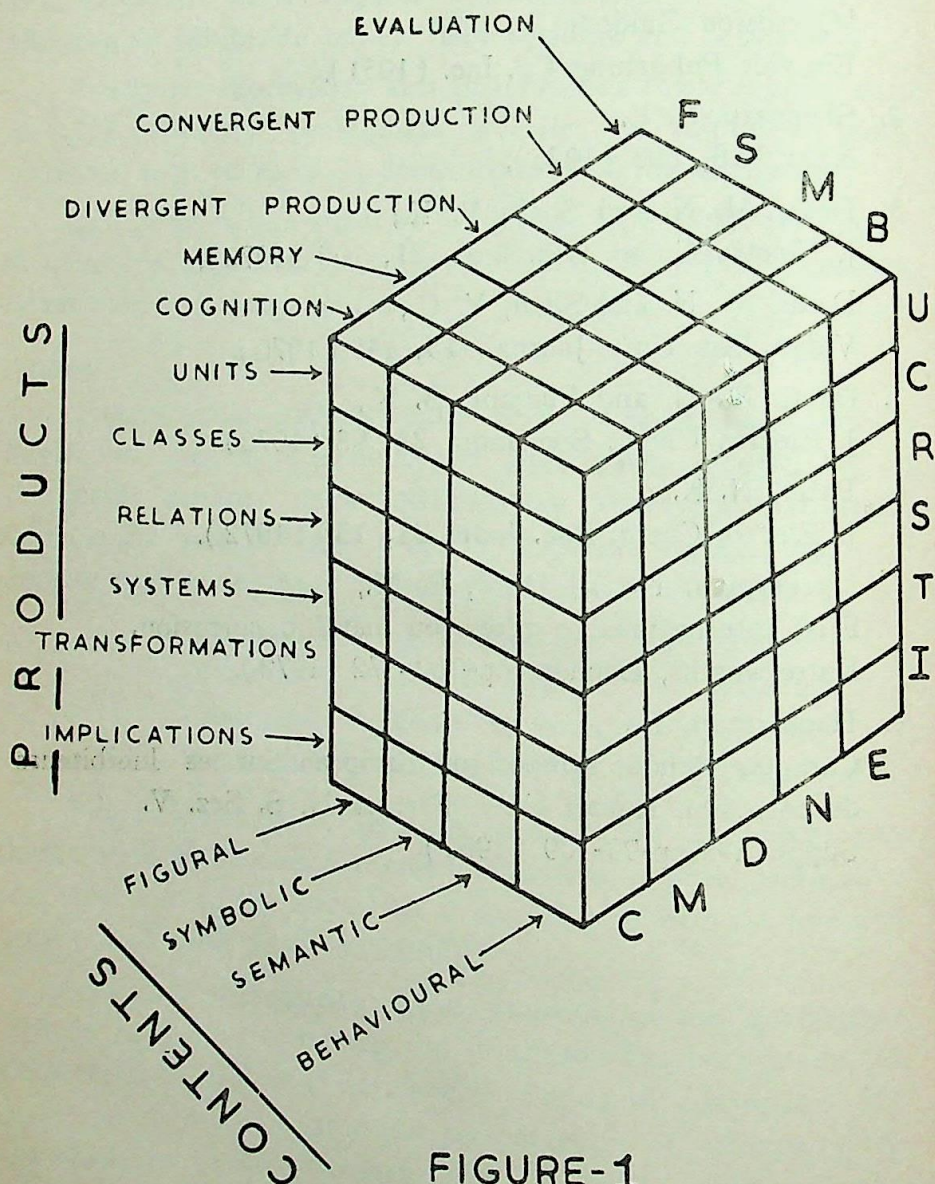   Suppl. n-3 pp-99-109 (1961).

OPERATIONS

FIGURE-1

STRUCTURE OF INTELLECT MODEL

SYNTHESIS OF 2–(SUBSTITUTED PHENYL)–4–(2″–HYDROXY/METHOXY–5″–METHOXY–4″–CHLORO/BROMO–PHENYL)–$\triangle^4$–6–ONE–HEXENE–1–ETHYL–CARBOXYLATE

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Condensations of acetoaceticester with chalkones derived from 4–chloro and 4-bromoquinacetophenone mono and dimethyl—ethers in presence of sodium ethoxide have been studied in this paper.

On account of the reactive nature of keto-ethylenic group —CH=CH—C—, chalkones have been found to give rise to various addition
$\overset{\|}{O}$

reactions with compounds containing reactive methylene group.[1] The chalkones readily condense with acetoaceticester to give 2, 4–(aryl-substituted)$\triangle^4$-6–one-hexene–1–ethyl–carboxylate.

The required ketones 4-chloro and 4-bromo-quinacetohenones and their mono and dimethyl ethers were prepared according to P. R. Shah and N. M. Shah.[2] The chalkones were prepared by condensing a variety of aldehydes with the above ketones using ethanolic alkali according to P. R. Shah and N. M. Shah.[3]

The following procedure was used for preparing the chalkone derivatives mentioned above.

The chalkone (0.01 mole) was added to solution of sodium (0.01 mole) in dry ethanol (20 ml) followed by ethyl acetoacetate (0.01 mole) and more ethanol (20 ml). The reaction mixture was then refluxed on water bath for 1 to 2 hours. It was then cooled and poured into ice+water

and acidified with cold hodrochloric acid. The product obtained was collected, dried and crystallised from ethanol or petrol ether (if pasty mass was obtained). The esters obtained are summarised in the following table I.
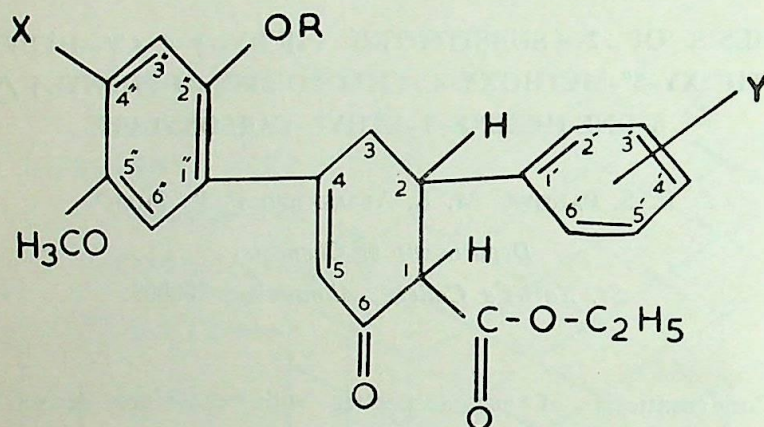

TABLE I

R=	X=	Y=	Molecular Formula	Melting Point °C	% Halogen Found	Cal.
H	Cl	H	$C_{22}H_{21}O_5Cl$	177	8.73	8.86
H	Br	H	$C_{22}H_{21}O_5Br$	185	17.78	17.98
—CH₃	Cl	H	$C_{23}H_{23}O_5Cl$	110	8.43	8.56
—CH₃	Br	H	$C_{23}H_{23}O_5Br$	65	17.28	17.43
H	Cl	4'-OCH₃	$C_{23}H_{23}O_6Cl$	135	8.03	8.24
H	Br	,,	$C_{23}H_{23}O_6Br$	166	16.69	16.85
—CH₃	Cl	,,	$C_{24}H_{25}O_6Cl$	50	7.75	7.98
—CH₃	Br	,,	$C_{24}H_{25}O_6Br$	45	16.14	16.36
H	Cl	4'-Chloro	$C_{22}H_{20}O_5Cl_2$	152	16.21	16.32
H	Br	,,	$C_{22}H_{20}O_5ClBr$	97	23.78	24.08
—CH₃	Cl	,,	$C_{23}H_{22}O_5Cl_2$	50	15.39	15.81
—CH₃	Br	,,	$C_{23}H_{22}O_5ClBr$	66	23.22	23.41
H	Cl	2', 4'–dichloro	$C_{22}H_{19}O_5Cl_3$	205	22.19	22.68
H	Br	,,	$C_{22}H_{19}O_5Cl_2Br$	169	29.01	29.38
—CH₃	Cl	,,	$C_{23}H_{21}O_5Cl_3$	52	21.79	22.03
—CH₃	Br	,,	$C_{23}H_{21}O_5Cl_2Br$	73	28.24	28.57

Synthesis of........

R=	X=	Y=	Molecular Formula	Melting Point°C	% Halogen Found	Cal.
H	Cl	3'–4'–methylene dioxy	$C_{23}H_{21}O_7Cl$	163	7.55	7.98
H	Br	,,	$C_{23}H_{21}O_7Br$	145	16.12	16.36
—CH$_3$	Cl	,,	$C_{24}H_{23}O_7Cl$	60	7.43	7.74
—CH$_3$	Br	,,	$C_{24}H_{23}O_7Br$	90	15.67	15.91
H	Cl	4'–N(CH$_3$)$_2$	$C_{24}H_{26}O_5NCl$	128	7.65	7.99
H	Br	,,	$C_{24}H_{26}O_5NBr$	110	16.14	16.40
—CH$_3$	Cl	,,	$C_{25}H_{28}O_5NCl$	77	7.29	7.76
—CH$_3$	Br	,,	$C_{25}H_{28}O_5NBr$	83	15.67	15.93
H	Cl	2'-hydroxy	$C_{22}H_{21}O_6Cl$	220	8.33	8.55
H	Br	,,	$C_{22}H_{21}O_6Br$	167	16.98	17.36
—CH$_3$	Cl	,,	$C_{23}H_{23}O_6Cl$	97	8.04	8.25
—CH$_3$	Br	,,	$C_{23}H_{23}O_6Br$	109	16.57	16.85
H	Cl	2'-methyl	$C_{23}H_{23}O_5Cl$	112	8.44	8.56
H	Br	,,	$C_{43}H_{23}O_5Br$	119	17.12	17.43
—CH$_3$	Cl	,,	$C_{24}H_{25}O_5Cl$	87	7.88	8.05
—CH$_3$	Br	,,	$C_{24}H_{25}O_5Br$	92	16.63	16.91

Hydrolysis and decarboxylation of many esters reported in table I was tried and in each case a pasty product was obtained which could not be crystallised.

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C–n–PROPYLATION OF RESACETOPHENONE

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Abstract

[*C–n*–Propylation of resacetophenone has been studied using *n*–propyl bromide, and methanolic potassium hydroxide when 2–hydroxy–3–*n*–propyl–4–*n*–propoxy–acetophenone and 2-hydroxy-4-*n*-propoxyacetophenone were obtained. To establish the structure of the former compound, it was depropylated and the compound obtained was oxidised to carboxylic acid which on decarboxylation gave 2–*n*-propylresorcinol.]

Various workers[1,2,3] have studied the *C*–alkylation of different phenols using an excess of alkyl halides and potassium hydroxide. Kananiwa[4] studied *C*–iso-amylation-and *C*–*n*-butylatian of resacetophenone and ethylation and *n*-butylation of resbutyrophenone using sodium in ethyl alcohol and corresponding alkyl halides. In the present work *C*–*n*-propylation of resacetophenone has been studied. It is observed that *C*–substitution also takes place with *n*-propyl halide in presence of alcoholic potassium hydroxide.

Resacetophenone (I: $R_1 = R_2 = H$) on treating with an excess of *n*–propyl bromide and potassium hydroxide gave 2-hydroxy-3-*n*-propyl-4-*n*-propoxyacetophenone (I: $R_1 = R_2 = Pr^n$) along with 2-hydroxy-4-*n*-propoxyacetophenone (I : $R_1 = Pr^n$; $R_2 = H$). The former on depropylation gave 2, 4-dihydroxy-3-*n*-propylacetophenone (I: $R_1 = H$; $R_2 = Pr^n$). 2–Hydroxy-3-*n*-propyl 4-*n*-propoxyacetophenone was oxidised to 2-hydroxy-3-*n*-propyl-4-*n*-propoxybenzoic acid (II : $R_1 = R_2 = P_r^n$). The structure of 2, 4 dihydroxy-3-*n*-propylacetophenone was established by its oxidation to 2, 4-dihydroxy-3-*n*-propylbenzoic acid (II : $R_1 = H$; $R_2 = Pr^n$) using the method of King[5]. 2, 4-Dihydroxy-3-*n*-propylbenzoic acid was decarboxylated to the known 2-*n*-propylresorcinol[6].

Figure
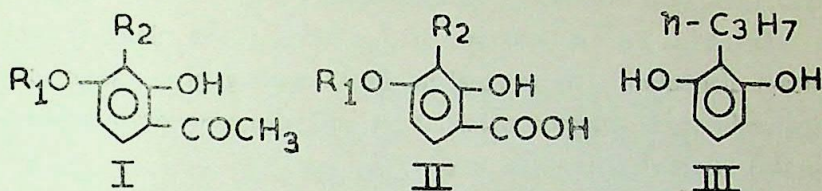
C–n. Propylation of Resacetophenone

2-Hydroxy-3–n-propyl–4–n-propoxyacetophenone (II : $R_1 = R_2 = Pr^n$) : Resacetophenone[1] (15g. : 1 mole) was dissolved in methanolic potassium hydroxide (17.0 g. : 3 mols. in 125 ml.), *n*-propyl bromide (43.0g : 3.5 mols) was added and the mixture left overnight, when some solid separated. It was refluxed on a steam–bath for 5 hrs, methanol and excess of *n*–propyl bromide were removed by distillation. The residue was acidified and steam distilled when 2-hydroxy-4-*n*–propoxyacetophenone was obtained, m.p. 25°. Eijkaman, Bergema and Hennard[7] gave the same m.p.

The solution that remained after steam distillation was extracted with ether. The ether was removed and the residue was distilled under reduced pressure when 2-hydroxy-3-*n*-propyl-4-*n*-propoxyacetophenone was obtained as pale yellow liquid, b.p. 110°/12 mm.

Analysis : Found C 70.8, H 8.3.

$C_{14}H_{20}O_3$ requires C 71.2, H 8.5 per cent.

It gave a 2, 4 dinitrophenylhy drazone, red crystals, m.p. 135° C.

Oxidation of 2-hydroxy-3-n-propyl 4-n- propoxyacetophenone : *2-Hydroxy-3-n-propyl 4–n propoxybenzoic acid* (II : $R_1 = R_2 = Pr^n$) :

The oxidation was carried out by the method of King. 2-Hydroxy-3-*n*-propyl-4-*n*-propoxyacetophenone (0.4 g.), iodine (0.2 g.) and pyridine (2 ml.) were heated on a boiling water bath for two hours. On keeping it overnight in a refrigerator, a complex separated. It was washed with ether and hydrolysed by heating with a solution of alkali (10 ml : 4 per cent) on a boiling water bath for one hr. The solid, obtained on acidification, was crystallised from ethanol, colourless needles. m.p. 163°.

Analysis : Found C 65.3; H 7.3

        $C_{13}H_{18}O_4$ requires C 65.5, H 7.5 per cent.

Depropylation of 2–hydroxy-3–n–propyl–4–n–propoxyacetophenone : *2 : 4 Dihydroxy-3–n–propylacetophenone* (*I : $R_1 = H$: $R_2 = Pr^n$*) :

A mixture of 2-hydroxy-n-propyl-4-n-propoxyacetophenone (1.2 g), glacial acetic acid (10 ml.) and hydrobromic acid (5 ml.: 48 per cent) was refluxed on an oil bath at 140° for 3 hrs. It was diluted and subjected to steam–distillation. The residual liquid on cooling gave a solid which was crystallised from ethanol when 2 : 4 dihydroxy-3-n-propylacetophenone separated, colourless needless, m.p. 127°.

Analysis : Found C 67.6, H 7.4

$C_{11}H_{14}O_3$ requires C 68.0; H 7.2 per cent.

It gave a 2, 4 dinitrophenylhydrazone, red crystals, m.p. 226°.

Oxidation of 2, 4 dihydroxy–3–n–propylacetophenone :

2, 4-*Dihydroxy*-3-*n-propylbenzoic acid* (*II* : $R_1 = H; R_2 = P^n$):

2, 4–Dihydroxy-3-n-propylacetophenone (0.39 g.) was oxidised using iodine (0.2 g.) and pyridine (2 ml.) to 2:4 dihydroxy 3-n-propylbenzoic acid which was crystallised from ethanol as colourless m.p. 157°.

Analysis : Found C 60.9; H 5.9

$C_{10}H_{12}O_4$ requires C 61.2; H 6.1 per cent

Decarboxylation of 2, 4–dihydroxy–3–n–propylbenzoic acid :

2-*n–Propylresorcinol* (III) :

2, 4-Dihydroxy-3-n-propylbenzoic acid (0.5 g.) was dissolved in quinoline (5 ml.), finely divided copper (0.5 g.) added and the mixture was heated on an oil-bath at 200–210° for 30 min. The solution was filtered from the copper powder and quinoline was removed by adding 2N hydrochloric acid. It was extracted with ether, the ether extract was washed with sodium bicarbonate solution, then with water and dried. The ether was evaporated. It was crystallised from ethanol, colourless, needless, m.p. 95°. Russel, Fyre and Mauldin[6] gave the same m.p.

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Cu²⁺ CHELATES OF THE SCHIFF BASES OF THE KETONES 2 : 5 di-OH-3-Br-ACETOPHENONE, 2 : 5 di-OH-3-Br-BENZOPHENONE AND 2:5di-OH-3-Br-PROPIOPHENONE WITH ETHYLENE DIAMINE

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Abstract

The ligands bis (2 : 5 di-OH-3-Br-acetophenone) -en, (H_2SB), bis (2:5 di-OH, 3-Br-benzophenone)-en (H_2SB'), and bis (2 : 5 di-OH-3-Br-propiophenone)-en, (H_2SB''), are used here to study their complex-forming behaviour with Cu^{2+}. It is found by analytical, magnetic, conductivity and spectral data that the metal ion gives 1:1 complexes with all the three Schiff bases and can be represented as CuSB, CuSB' and CuSB'' respectively. All the three complexes are assigned a square planar structure.

Introduction :

It was decided to study the Cu^{2+} complexes with Schiff bases formed by condensing 2 : 5 di-OH-3-Br-acetophenone, 2 : 5 di-OH-3-Br-benzophenone and 2 : 5 di-OH-3-Br-propiophenone with ethylene diamine. Cu^{2+}-complexes with the unbrominated Schiff bases[1] (all the three) were recently shown to have a square planar structure. We find that the Cu^{2+}-complexes under study are analogous.

1).

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Experimental :

(*a*) **Preparation of Schiff bases :**

The Schiff bases 2 : 5 di–OH–3–Br–acetophenone, 2 : 5 di–OH–3–Br–benzophenone and 2 : 5 di–OH–3–Br propiophenone with ethylene diamine were prepared by condensing 2 moles of bromo–ketone with one mole of ethylene diamine in presence of absolute ethyl alcohol by refluxing the mixture for one hour. The brownish–yellow Schiff bases formed were recrystallised from chloroform when they showed the m.pts. of 310°, 168° and 296° C respectively.

(*b*) The Cu^{2+}–complexes of Schiff bases were prepared in the usual manner[1] and were finally recrystallised from D.M.F. All the Cu^{2+} complexes are dark brown in colour. They are insoluble in water and sparingly soluble in chloroform and ethyl alcohol. They are stable in air up to a temperature of 150° C.

(*c*) **Analysis of Chelates :**

The chelates were broken by a small quantity of perchloric acid. The percentage of metal ion in each chelate was estimated by standard analytical methods[2]. Bromine in each case was estimated by Kay and Haywood[3] method. The mol. wts. determined cryoscopically using camphor as a solvent, showed the chelates to be monomeric i.e. the chelates could be represented as CuSB, CuSB′ and CuSB″ respectively. Their conductivity in D.M.F. was very low, proving their non-electrorytic nature. The results of several such determinations of each complex are given in Table No. 1. From this Table, it can be seen that the experimental work fits very well with the results considering the complexes to be 1 : 1 so that the ligands are quadridentate. Hence the structures of the complexes can be written as under :
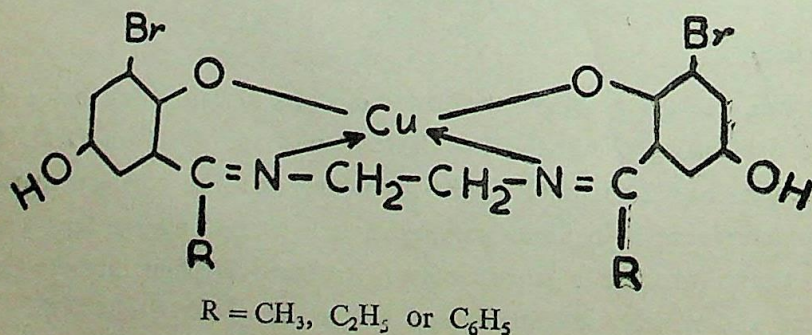

$$R = CH_3, \; C_2H_5 \; \text{or} \; C_6H_5$$

TABLE I

Structure :

Sr.No.	Schiff chelates	Amount taken in grams	Metal Estimation	
			Found%	Expected%
1.	CuSB	0.500	11.50%	11.58%
2.	CuSB'	0.500	9.69%	9.47%
3.	CuSB″	0.500	11.06%	11.04%

Bromine Estimation		Mol. wts.		Molar conductance
Found	Expected	Found	Expected	mhos c_m^2 mole^{-1}
29.79%	29.18%	560	547.54	20
		529		
		528		
28.72%	27.78%	660	671.54	23
24.68%	23.83%	660		
		649.5		
		563.2	575.54	25
		574.4		
		574.4		

(d) Magnetic Moment :

The magnetic moment determination shows the complexes to be paramagnetic with $\mu_{eff}=1.89$ B.M. for CuSB; $\mu_{eff}=2.18$ B.M. for CuSB' and $\mu_{eff}=2.12$ B.M. for CuSB″ at room temp. It may be corelated with the "spin only" formula for calculating the magnetic moment $\mu_{eff}=\sqrt{n(n+2)}$. The value for one unpaired electron (n=1) would, on this basis, be 1.73 B.M. The excess over this value found for the present complexes can be attributed to the spin–orbit coupling.[4, 5, 6]. It is presumed that all the three complexes are square planar in structure. The magnetic data is collected in Table No. II.

(e) Electronic Spectra :

The absorption spectra of all the three complexes were taken in D.M.F. by using Spectronic –20 and are given in Table No. II

TABLE II

Sr. No.	Cu^{2+} Chelates	Maximum λ (nm)	ε	$Xm.10^6 c.g.s.$	μeff (B.M.) at $37^0 C$
1.	CuSB	620	210	1429	1.89
		540	460		
		410	3000		
2.	CuSB'	620	320	1596.98	2.18
		540	740		
		420	5100		
3.	CuSB''	620	325	1525.83	2.12
		540	630		
		420	4900		

CuSB:–There are three absorption maxima, one at 620 nm ($\varepsilon = 210$), second at 540 nm ($\varepsilon = 460$) and the third at 410 nm ($\varepsilon = 3000$). The first two, being weak are d–d–transitions and may be ascribed to the electronic transitions[7, 8] :

$$(1)\ a_{1g}^2\ b_{1g}^1 \rightarrow a_{1g}^2\ b_{1g}^1\ i.e.\ {}^2A_{1g} \leftarrow {}^2B_{1g}.$$

$$(ii)\ e_g^4\ b_{1g}^1 \rightarrow e_g^3\ b_{1g}^2\ i.e.\ {}^2E_g \leftarrow {}^2B_g.$$

The band at 410 nm has intermediate intensity characteristic of a charge transfer band. CuSB' and CuSB'':— The spectra here are more or less similar to the one with CuSB, with regard to both position and intensity and hence must have similar origins.

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Fe³⁺ CHELATES OF BROMOKETOXIMES

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Abstract

The chelate–forming behaviour of ligands

(*i*) 2–OH–3–Br–5–Me–acetophenonoxime (HL):

(*ii*) 2–OH–3–Br–5–Me–propiophenonoxime (HL′) and

(*iii*) 2-OH-3-Br-5-Me-benzophenonoxime (HL″) with Fe^{3+} is studied. The complexes were found to possess 1 : 3 stoichiometry on the basis of analytical and molecular wt. determination. The magnetic moments show them to be high-spin octahedral complexes. Electronic spectra are consistent with such assignments of structure.

Much research work is being done nowadays on the preparation, properties and structures of metal chelates of oximes[1]. It was decided to study the complexes of Fe^{3+} with the following ligands : (*i*) 2–OH–3–Br–5–Me–acetophenonoxime (HL); (*ii*) 2–OH–3–Br–5–Me–propiophenonoxime (HL′) and (*iii*) 2-OH-3-Br-5-Me-benzophenonoxime (HL″).

A. Experimental :

(*a*) Preparation of Oximes : The ketones, 2-OH-5-Me-acetoph-enone, 2-OH-5-Me-propiophenone and 2-OH-5-Me-benzophenone were obtained by Fries[2] migration of p-cresyl acetate, p-cresyl-propionate and p-cresyl benzoate, respectively. They were next brominated in acetic acid solution. The bromoketones were then converted into their oximes by refluxing for some two hours with hydroxylamine hydrochloride in absolute alcohol[3]. The pinkish-white oximes were recrystallised from absolute alcohol. Their m.pts. were 155° C, 156° C and 158° C respectively.

(*b*) Preparation of the Fe³⁺ Chelates :

$FeCl_3, 6H_2O$ (analar) solution in water was refluxed with the oxime ligands in presence of an acetate buffer of pH=6 to 7 for some two hours. The dark ruby-red chelates formed were washed with water and finally with alcohol and dried at 110°-115° C. All the metal-chelates were recrystallised from chloroform. They are insoluble in water, slightly soluble in absolute alcohol and readily soluble in chloroform, benzene, etc. They are stable in air upto a temperature of 140° C.

B. Analysis of Fe³⁺-Chelates :

The chelates were decomposed by a small quantity of con. sulphuric acid. The percentage of Fe^{+3} in each case was estimated by standard analytical method[4]. Bromine in each case was estimated by Kay and Haywood[5] method. The mol. wts., determined cryoscopically, showed them to be monomers. They are all non-electrolytes[6] as shown by their very low conductivity in chloroform. The 1:3 stoichiometry was confirmed in all the three cases by Job's method. For this, the chelates where extracted in chloroform and their optical densities were measured. In each case the clear maximum was found to be at 25% of $\frac{M}{M+L}$ giving a 1 : 3 comp: osition for the chelates. These and other results are given in Table I.

TABLE 1

Sr.No.	Complexes	Amount taken in (grams)	Metal Estimation		Br-Estimation		Molecular wts.		Molar Conductance (mhos-cms²-mole⁻¹)
			Found%	Expected%	Found%	Expected%	Found	Expected	
1.	FeL_3	0.5	6.96%	7.11%	30.12%	30.56%	768.0	784.85	10
2.	FeL_3'	0.5	6.66%	6.76%	29.41%	29.03%	844.8	826.85	10
3.	FeL_3''	0.5	5.59%	5.75%	25.07%	24.72%	960.0	970.85	10

The ligands are, thus, bidentate as expected. The ferric chelate, therefore, is given the following structure:

$$R = -CH_3; -C_2H_5 \text{ AND } -C_6H_5$$
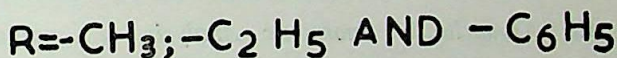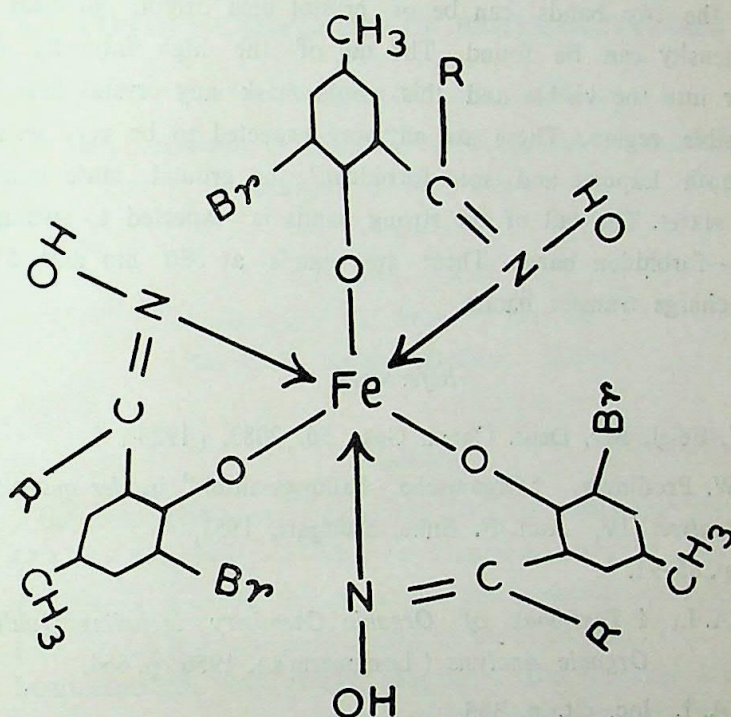
The three chelates have the following magnetic moments:

No.	Chelates	$\chi_M^{Corr.} \times 10^{-6}$ c.g.s.	μ eff (B.M.)
1.	FeL_3	14292	5.96
2.	FeL_3'	14323	6.0
3.	FeL_3''	13040	5.7

The magnetic susceptibilities were determined for the solids at room temperatures by the Gouy method.

These values for magnetic moment indicate five unpaired electrons. These complexes are, therefore, considered octahedral in structure. The orbital configuration[6] is the high spin type $t^3_{2g}\ e^2_g$, the ground state $^6A_{1g}$.

All these dark–red solids have a broad absorption band in the visible. It has not much structure in it. Shoulders around 580 nm ($\epsilon = 2500$) and 510 nm ($\epsilon = 3100$) can be identified. In view of the high intensity, neither of the two bands can be of crystal field origin. No clear band of low intensity can be found. The tail of the high intensity bands extends far into the visible and this would mask any crystal field bands in the visible region. These are any way expected to be very weak as they are both Laporte and spin forbidden[7], the ground state being the only spin sextet. The tail of the strong bands is expected to swamp any such spin—forbidden bands. These two bands at 580 nm and 510 nm could be charge transfer bands.

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CO (III) COMPLEXES OF BROMOKETOXIMES

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Abstract

The metal chelates of the ion Co (III) with the ligands
(I) 2-OH-3-Br-5-Me—acetophenonoxime, (HL),
(II) 2-OH-3-Br-5-Me-propiophenonoxime, (HL'), and
(III) 2-OH-3-Br-5-Me-benzophenonoxime, (HL") have
been studied. Analytical, magnetic and spectral studies
are carried out to determine their stoichiometry and
structures.

2-OH—5-Me-acetophenonoxime was used[1] to study its
complex with Co (III). It was found to give a 1:3 complex
which was slightly paramagnetic. Here it was decided to study
the complexes of Co (III) with the following ligands :

(1) 2-OH-3-Br-5-Me-acetophenonoxime, (HL),
(2) 2-OH-3-Br-5-Me-propiophenonoxime, (HL') and
(3) 2-OH-3-Br-5-Me-benzophenonoxime, (HL ").

The materials used were of Analar quality.

Experimental :

Preparation of Oximes :

The ketones, 2-OH—5-Me-acetophenone, 2-OH-5-Me
propiophenone and 2-OH-5-Me-benzophenone were obtained

by Fries[2] migration of p-cresylacetate, p-cresyl propionate and p-cresyl benzoate respectively. They were next brominated in acetic acid solution with bromine. The bromoketones were then converted into their oximes by refluxing them for two hours with hydroxylamine hydrochloride in absolute alcohol. The pinkish-white oximes were recrystallised from alcohol. Their m.pts. were 155°C, 146°C and 158°C for HL, HL' and HL'' respectively.

Preparation of Co(III) Chelates :

Cobalt nitrate was dissolved in water and H_2O_2 and NaOH were added to it to oxidise Co(II) to Co(III). The Co(OH)$_3$ which was precipitated was dissolved in minimum quantity of acetic acid and an alcoholic solution of the ligands was quickly added to it. The mixture was refluxed for two hours while passing air through it. The pH of the solution during refluxing was maintained between 6 to 7 by means of an acetate buffer. The reddish-brown chelates formed were washed with water to remove excess metal and finally with alcohol to remove unreacted ligands. They were dried at 110°C. They are insoluble in water, slightly soluble in alcohol and readily soluble in chloroform, benzene etc. All these chelates were recrystallised from chloroform. They are stable in air upto a temperature of 140°C.

Analysis of Chelates :

The chelates were decomposed by a small quantity of con. sulphuric acid. The percentage of cobalt in each case was determined by standard analytical method[3]. Bromine was estimated by Kay and Haywood[4] method. The metal ligand ratio was found in each case to be 1:3. The mol. wts., determined cryoscopically, showed them to be monomers. They are all non-electrolytes as shown by their very low conductivity in D.M.F. solution. The 1:3 composition was confirmed by job's method of continuous variation. For this purpose, they were extracted in benzene and optical densities of different concentrations were measured. In all the three cases the graphs showed

Co (III) Comlexes of......

clear maxima in optical density at 25 % M/M + L. From these data, it is concluded that all the three chelates are monomers and can be represented as CoL_3. The details of the analysis are given in Table No. I.
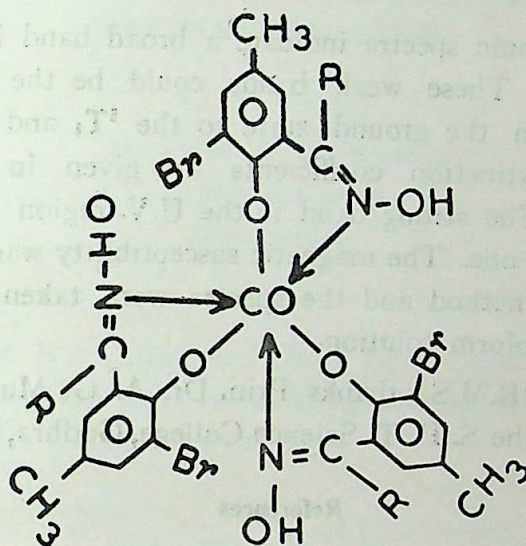
$$R = CH_3; \quad C_2H_5; \quad AND - C_6H_5$$

Table No. I

Sr. No.	Chelates →	Metal Estimation% Found%	Expected%	Br. Estimation% Found%	Expected%	Mol. Wts. Found%	Ex-pected	Mol. Conduct ance mhos cm²/ mole
1.	CoL_3	7·54%	7·48%	30·17%	30·46%	782·2	787·9	10
2.	CoL_3'	7·25%	7·10%	28·68%	28·91%	826·2	829·9	10
3.	CoL_3''	6·16%	6·07%	24·93%	24·64%	960·0	973·0	10

Magnetic and Spectral Properties :

Table No. 2.

Sr. No.	Compou s	dnχ Corr M	c.g.s. Units	λmax.
1.	CoL_3	-411.94×10^{-6}		615 nm (84)
2.	CoL_3'	-284.77×10^{-6}		625 nm (105)
3	CoL_3''	-164.35×10^{-6}		640 nm (22).

All the complexes are diamagnetic confirming valency three for cobalt in these complexes. The diamagnetism also indicates a t_{2g}^6 electronic configuration giving a strong field $^1A_{1g}$ ground term for the complexed metal ion.

The electronic spectra indicate a broad band in each case in the visible. These weak bands could be the spin-allowed transitions from the ground state to the $^1T_1$ and $^1T_2$ excited states. The extinction coefficients are given in brackets in Table No. II. The strong band in the U.V. region seems to be an intra-ligand one. The magnetic susceptibility was determined by the Gouy method and the spectra were taken on Spectronic-20 in chloroform solution.

One of us (R.M.S) thanks Prin. Dr. A. G. Munshi and the Authorities of the S. P. T. Science College, Godhra, for facilities.

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A CURIOUS COSMOLOGICAL SOLUTION OF
EINSTEIN'S EQUATIONS

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Misra and Radhakrishna (1962) have discussed a vacuum metric in connection with electromagnetic fields of cylindrical symmetry. This metric is given by

$$ds^2 = e^{\frac{m^2 r^2}{4} + mt} (dt^2 - dr^2) - r^2 e^{mt} d\varphi^2 - e^{-mt} dz^2 \tag{1}$$

where r, φ, z are cylindrical polar coordinates and m is a constant. The object of the present note is to report on a universe filled with perfect fluid which reduces to the empty space-time described by (1) when pressure and density become zero. The geometry of this universe is described by the line-element

$$ds^2 = e^{\alpha-\beta} (dt^2 - dr^2) - r^2 e^{-\beta} d\varphi^2 - e^{\beta} dz^2 \tag{2}$$

where α is a function of r alone and β is a function of t alone.

The field equations of general relativity for a perfect fluid distribution

$$R^l_k - \tfrac{1}{2} R \delta^l_k + \lambda \delta^l_k = -8\pi [(p + \rho) v^l v_k - p \delta^l_k] \tag{3}$$

are satisfied if

$$v^1 = v^2 = v^3 = 0, \quad v^4 = e^{\frac{\beta-\alpha}{2}} \tag{4}$$

and

$$\alpha = k r^2 + l, \quad \beta = -mt + n \tag{5}$$

where l, m, n, k are constants of integration and 1, 2, 3, 4 correspond to r, φ, z and t respectively.

The pressure p and density ρ are given by

$$8\pi p = e^{\beta-\alpha}\left(k - \frac{m^2}{4}\right) + \lambda \qquad (6)$$

$$8\pi \rho = e^{\beta-\alpha}\left(k - \frac{m^2}{4}\right) - \lambda$$

In order to have $\rho > p$, we have to choose λ as negative. If we set $\lambda = 0$ we obtain $p = \rho$ which is not desirable from physical point of view. This is the main reason for introducing the cosmological term. The constants k and m have to satisfy the inequality $4k > m^2$.

We $4k = m^2$ we obtain $p + \rho = 0$. As p is non-negative and ρ is positive $p + \rho = 0$ implies $p = 0$ and $\rho = 0$ which further implies $\lambda = 0$. In this case we get the empty space-time described by (1).

The scalar of expansion θ and the non vanishing components of the shear tensor q_{ik} are given by (3)

$$\theta = \frac{m}{6}\,e^{\frac{\beta-\alpha}{2}} \qquad (7)$$

and

$$q_{11} = -\frac{m}{3}\,e^{\frac{\beta-\alpha}{2}},\; q_{22} = -\frac{m}{3}\,e^{\frac{-(\alpha+\beta)}{2}},\; q_{33} = -\frac{m}{3}\,e^{\frac{3\beta-\alpha}{2}} \qquad (8)$$

In the present note we have chosen the cosmological constant λ as negative in order to make $\rho > p$. In the standard relativistic cosmological models Eddington and others interpreted the positive λ as representing a repulsive force responsible for the expansion of the universe. Viewed in this sense a negative λ must represent an attractive force (which helps the gravitational force). Hence it seems more appropriate to think the present cylindircal model as one imploding on the axis of symmetry. In such a case θ given in equation (7) will be negative which may easily be met by taking m as negative. The presence of shear is not surprising since it is a characteristic of every cylindrically symmetric model.

The acceleration vector $f_i = v_{i;k}v^k$ for the universe discussed above is given by

$$f_i = (-kr,\,0,\,0,\,0) \qquad (9)$$

Thus the stream lines of the perfect fluid distribution filling the universe are not geodesics. The expression for force given in equation (9) is a bit disturbing. Here, the force is attractive but proportional to the radial distance which means that a material particle far away from the axis of symmetry is being pulled with a far greater force then the particle nearer to the axis. This is a curious feature of our solution. However if we put $m=0$, we obtain a static universe in which the stream lines of the perfect fluid filling it are not geodesics.

The author is highly indebted to Professor P. C. Vaidya and Dr. M. Misra for many helpful discussions.

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PROPAGATION OF ELECTROMAGNETIC RADIATION IN A NON-UNIFORM UNIVERSE

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Summary

The propagation of electromagnetic radiation in a non-uniform model is considered. It is shown that the full retarded solutions are not consistent and the full advanced solutions are consistent in such a cosmological model.

1. Introduction :

Goodinson (1969) has considered the line-element

$$ds^2 = \frac{e^f}{2\sqrt{r}} \left(dt^2 - dr^2 \right) - r \left(d\phi^2 + dz^3 \right) \tag{1.1}$$

in connection with null electromagnetic radiation where r, ϕ, z are cylindrical polar co-ordinates and f is a function of the retarded time $u \equiv t - r$.

Patel (1973) has discussed a non-uniform universe whose geometry is described by the line-element,

$$ds^2 = \frac{e^a}{2\sqrt{r}} \left(dt^2 - dr^2 \right) - re^\beta \left(d\phi^2 + dz^2 \right) \tag{1.2}$$

where α and β are functions of t alone. For this universe the functions α and β are given by

$$e^\alpha = k^2 \, e^{\frac{3}{2}\beta} \quad \text{and} \quad e^\beta = At + B \tag{1.3}$$

where A, B and k are constants. Without any loss of generality B may be put equal to zero (time-translation) and A may be put equal to unity (time-rotation).

Therefore

$$e^{\alpha} = k^2 e^{\frac{3}{2}\beta} \text{ and } e^{\beta} = t \qquad (1.4)$$

The object of the present investigation is to study the flow of null electromagnetic radiation in the universe described by (1.2).

2. Field Equations :

Consider a Riemannian 4-space described by the line-element,

$$ds^2 = \frac{e^{\alpha+f}}{2\sqrt{r}} (dt^2 - dr^2) - re^{\beta} (d\varphi^2 + dz^2) \qquad (2.1)$$

where a and β are functions of time t alone and f is a function of $t \pm r$. The radiation is retarded or advanced according as f is a function of $t-r$ or $t+r$ respectively. In what follows wherever the symbol $\mp$ (or $\pm$) occurs, always the upper sign corresponds to the retarded solution and the lower one stands for advanced solution. The non-vanishing components of Ricci tensor R^i_k for the metric (2.1) are given by

$$R^1_1 = \sqrt{r} \; e^{-(\alpha+f)} \left[\ddot{\alpha} + \dot{\alpha}\,\dot{\beta} - f' \left(\pm\frac{1}{r} - \dot{\beta} \right) \right]$$

$$R^2_2 = R^3_3 = \sqrt{r} \; e^{-(\alpha+f)} [\, \ddot{\beta} + \dot{\beta}^2_\shortmid \,] \qquad (2.2)$$

$$R^4_4 = \sqrt{r} \; e^{-(\alpha+f)} \left[o\dot{2} + \ddot{\alpha} + 2\ddot{\beta} - \dot{\alpha}\,\dot{\beta} - f' \left(\dot{\beta} \mp \frac{1}{r} \right) \right]$$

$$R^1_4 = -R^4_1 = \frac{1}{\sqrt{r}} e^{-(\alpha+f)} \left[\dot{\alpha} - \frac{3}{2}\,\dot{\beta} + rf' \left(\frac{1}{r} \mp \dot{\beta} \right) \right]$$

where the indices, 1, 2, 3, 4 correspond to r, ϕ, z and t respectively. Here and in what follows an overhead dot denotes differentiation with regard to t and

$$f' = \frac{d}{d(t \mp r)} (f).$$

To study the propagation of null radiation in the non-uniform universe discussed by Patel, we assume the distribution to be a mixture of perfect fluid and radiation. The energy memontum tensor for such a distribution can be chosen as

$$T^i_k = (p + \rho) v^i v_k - p\delta^i_k + \sigma w^i w_k \qquad (2.3)$$

$$v^i v_i = 1, \quad w^i w_i = 0$$

where p, ρ and σ are respectively the pressure, material density and radiation density. We use co-moving co-ordinates. Therefore

$$v^i = \left(0,\, 0,\, 0,\, e^{-\frac{(a+f)}{2}}\sqrt{2}\, r^{\frac{1}{4}}\right) \tag{2.4}$$

The null vector w^i can be taken as

$$w^i = e^{-(a+f)}(\pm 1, 0, 0, 1) \tag{2.5}$$

The field equations of general relativity are

$$R^i_k - \tfrac{1}{2}R\delta^i_k + \lambda\delta^i_k = -8\pi T^i_k \tag{2.6}$$

where λ is a cosmological constant. The result (2.2), (2.3), (2.4), (2.5) and (2.6) imply that

$$e^{a} = k^2 e^{\frac{3}{2}\beta} \text{ and } e^{\beta} = At + B \tag{2.7}$$

where A, B and k are constants of integration. The pressure p, density ρ and radiation density σ are given by

$$8\pi p = 2\sqrt{}\; {}^2 e^{-(a+f+2\beta)} + \lambda$$
$$8\pi \rho = 2\sqrt{}\; A^2 e^{-(a+f+2\beta)} - \lambda \tag{2.8}$$
$$8\pi \sigma = \frac{f'}{2}\left(\frac{A}{At+B} \mp \frac{1}{r}\right).$$

3. Discussion of the Solution :

In order to make $\rho > p$ we have to choose λ as negative. In the standard relativistic cosmological models, Eddington and other interpreted the positive λ as representing a repulsive force responsible for the expansion of the universe. Viewed in this sense a negative λ must represent an attractive force. Therefore we can think of the present cylindrical world model as one imploding on the axis of symmetry.

When $A = 0$, we obtain $p + \rho = 0$, $a = \text{constant}$, $\beta = \text{constant}$. As p is non-negative and ρ is positive, $p + \rho = 0$ implies $p = 0$ and $\rho = 0$ which further implies $\lambda = 0$. Thus in this case we get the Goodinson's solution for null electromagnetic radiation described by the metric (1.1).

It is clear from the expression for σ in (2.8) that f' changes sign even if the factor in the parenthesis does not change in sign.

To avoid such a situation we shall assume f to be monotonic. Then it is evident from the expression for σ that if we consider the propagation of retarded radiation, for some sets of values of r and t the radiation density σ becomes either zero or negative and therefore the model loses its physical significance. But in the case of advanced solution the model remains physically significant until we reach spatial or temporal infinity. Thus the full retarded solutions are not consistent and the full advanced solutions are consistent for this universe. As the present model is imploding on the axis of symmetry, the consistency of fully advanced solution is not surprising.

4. Acknowledgement :

The author wishes to thank the referee for his valuable comments.

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GENERALIZED CLOSED SETS AND ULTRACONNECTED SPACES

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Abstract

Some properties of generalized closed and generalized open sets with regard to separation axioms and Ultraconnected spaces are discussed.

1. Introduction

Norman Levine[1] (1970) has introduced the following definitions of generalized closed and generalized open (written henceforth as g-closed and g-open respectively) sets :

Definition 1 : A subset A of a topological space X is said to be g-closed if $\bar{A} \subset O$ whenever $A \subset O$ and O is open. (here $\bar{A}$ denotes the closure of A.)

Definition 2. A subset B of a topological space X is said to be g-open if its complement $\mathscr{C}B$ is g-closed.

N. Levine has discussed several properties of g-closed and g-open sets in his paper referred to above. He has shown that a set B of a topological space X is g-open iff $F \subset \mathscr{I}B$ whenever F is closed and $F \subset B$. Here $\mathscr{I}B$ denotes the interior of B.

Thron[2] has called a topological space X as a T_D–space if the derived set of every singleton of X is a closed set. He has shown that a topological space X is T_D iff for each $x \in X$ there exists a closed set F and an open set G such that $\{x\} = F \cap G$. He has also shown that every T_D–space is a T_0–space and every T_1–space is a T_D–space.

In the next two sections we shall discuss some properties of g–closed and g–open sets with regard to separation axioms and ultraconnected spaces.

2. g-Closed, g--Open Sets and Some Separation Axioms

Definition 3 : A topological space X is said to be a T'_D–space if the derived set of every singleton of X is a g-closed set.

It is easy to establish the following theorem :

Theorem 1 : A topological space X is T'_D iff for each $x \in X$ there exist a g-open set O and a closed set F such that $\{x\} = O \cap F$.

Proof : Easy and left to the reader.

We shalll now prove the following interesting result.

Theorem 2 : Every topological space is T'_D.

Proof : It is enough to prove that every singleton of a topological space is either closed or g-open.

Let X be a topological space and $x \in X$. Suppose $\{x\}$ is not closed. Then the only closed set contained in $\{x\}$ is the null set ϕ and ϕ is a subset of $\mathscr{D}\{x\}$. Therefore $\{x\}$ is g-open.

Definition 4 : A topological space X is said to be T''_D if for each $x \in X$ there exist a g-closed set F and an open set G such that $\{x\} = F \cap G$.

Obviously every T_D–space is T''_D but we shall see below that a T''_D–space need not be T_D.

Theorem 3 : Every topological space with finite number of open sets is T''_D.

Proof : Tet X be a topological space with only finite number of open sets. Let x be any point of X. If X is the only open set containing x then $\{x\}$ is g-closed and therefore nothing remains to be proved. Further if $\{x\}$ is open then also nothing remains to be proved. If x lies in proper open subsets of X then as there are only finite number of such sets x will lie in the smallest open set say G equal to the intersection of all open sets containing x. We may suppose here that $\{x\} \neq G$ as

$\{x\}$ is not open. Consider $F = \mathcal{C}G \cup \{x\}$. Now the only open set containing F is X because if O is a proper open set contaning F then such a set will contain x and hence G which is impossible Therefore F is g–closed and $G \cap F = \{x\}$.

Cor. 1. If X is a finite topological space then it is T''_D.

Poof : Obvious.

We shall now give an example of a topological space which is not T''_D.

Ex 1 : Let X be an infinite set and $\mathcal{J}$ be the cofinite topology on X. Let $\infty \notin X$. Let $X^* = X \cup \{\infty\}$. Let $\mathcal{J}^*$ be the family of subsets of X^* consisting of ϕ and sets like $O^* = O \cup \{\infty\}$ where O is an open non-void subset of X. Then $\mathcal{J}^*$ is clearly a topology on X^*.

We shall now prove that $(X^*, \mathcal{J}^*)$ is not a T''_D – space.

To prove this statement it is enough to show that $\{\infty\}$ cannot be put as the intersection of an open subset and a g–closed subset of $(X^*, \mathcal{J}^*)$.
$\{\infty\}$ is not g–closed as $\{\overline{\infty}\} = X^*$ and there are proper open subsets of X^* containing ∞.

If possible let $\{\infty\} = F^* \cap O^*$ where O^* is open in X^* and F^* is g–closed in X^*. Now O^* cannot be X^* as $\{\infty\}$ is not g–closed. So let O^* be a proper open subset of $(X^*, \mathcal{J}^*)$. Let $K = \mathcal{C}O^*$. Then F^* has to be $F^* = F \cup \{\infty\}$ where $F \subset K$. There are proper open sets containing F^* but $\overline{F}^* = X^*$. Therefore F^* is not g–closed and therefore there is a contradiction.

It may be noted that the space $(X^*, \mathcal{J}^*)$ is a T_0 – space.

Examples of finite topological spaces which are not T_0 – spaces are known. Such spaces, by Cor. 1, are T''_D – spaces. Therefore a T''_D – space need not be a T_0 – space and hence a T''_D – space need not be a T_D – space.

3. g-Closed Sets and Ultraconnected Spaces

Definition 5 : A topological space with no non-empty disjoint closed subsets is called an ultraconnected space (Steen and Seeback[3] (1970) and Norman Levine[4] (1965)).

It is known that—

(i) A topological space is ultraconnected iff the closures of distinct points always interest (Steen and Seeback, 1970)[3]

(ii) A topological space $(X, \mathcal{J})$ is ultraconnected iff every closed subset in X is connected (Norman Levine 1965)[4]

The poofs of the following three theorems are easy and therefore omitted:

Theorem 4 : A topological space, $(X, \mathcal{J})$ is ultraconnected iff for any closed set F of X there does not exist an open set other than X which contains F.

Theorem 5 : Let $\mathcal{J}_1$ $\mathcal{J}_2$ be two topologies for a non-empty set X and $\mathcal{J}_1 \subset \mathcal{J}_2$. If $(X, \mathcal{J}_2)$ is ultraconnected, $(X, \mathcal{J}_1)$ is ultraconnected.

Theorem 6 : Let $f : X \to Y$ be a one–one closed mapping and Y an ultraconnected space. Then X is also ultraconnected.

Theorem 7 : If Y is a g–closed subspace of an ultraconnected space X then Y is ultraconnected.

Proof : If Y is not ultraconnected, there exist nonempty closed subsets F'_1 and F'_2 of Y such that $F'_1 \cap F'_2 = \phi$. Let F_1 and F_2 be closed subsets of X such that $F_1 \cap Y = F'_1$ and $F_2 \cap Y = F'_2$. Then $F_1 \cap F_2 \cap Y = \phi$. Thus $Y \subset \mathcal{C}(F_1 \cap F_2) = O$ say. O is open in X. Also Y is g–closed. Therefore $\bar{Y} \subset \mathcal{C}(F_1 \cap F_2)$. Thus $F_1 \cap F_2 \cap \bar{Y} = \phi$. If $F_1 \cap F_2 = \phi$, X ceases to be ultraconnected. If $F_1 \cap F_2 \neq \phi$ then $F_1 \cap F_2$ and $\bar{Y}$ are two closed non-empty disjoint subsets of X which contradicts the fact that X is ultraconnected. Thus Y is ultraconnected.

Corollary 2 : Every closed subspace of ultraconnected space is ultraconnected.

Theorem 8 : If A is a g–closed and ultraconnected subset (ultraconnected as a subspace) of a topological space X and $A \subset B \subset \bar{A}$, then B is g–closed and ultraconnected.

Proof : As A is g–closed and $A \subset B \subset \bar{A}$, B is g–closed (Norman Levine, 1970). If B is not ultraconnected, there exist two closed non–empty subsets F_1 and F_2 in B such that $F_1 \cap F_2 = \phi$. Let us define $F'_1 = F_1 \cap A$ and $F'_2 = F_2 \cap A$. Now $F'_1 \cap F'_2 = \phi$. There is no non–empty closed set of B contained in $B-A$ (Norman Levine, 1970). Thus it is clear that F_1 and F_2 are not contained in $B-A$. Therefore F_1 and F_2 contain points of A. Thus F_1' and and F'_2 are non–empty. Moreover F'_1 and F'_2 are closed in A. This implies that A is not ultraconnected which is a contradiction. Hence B is ultraconnected.

Corollary 3 : If A is a g–closed ultraconnected subset of a topological space X, $\bar{A}$ is g–closed and ultraconnected.

Corollary 4 : A topological space is ultraconnected if it has a dense subset which is g–closed and ultraconnected.

Theorem 9 : An ultraconnected space is always a T''_D-space.

Proof : Let x be any point of an ultraconnected space X. If X is the only open set containing x, then $\{x\}$ is g–closed and therefore $\{x\}$ can be expressed as $\{x\} \cap X$ where $\{x\}$ is g–closed and X is open. If there is a proper open set G containing x then $F_0 = \complement G$ is a closed proper subset of X. Let $F = \{x\} \cup F_0$. As X is ultraconnected, the only open set containing F_0 is X. Therefore the only open set containing F is X. Therefore F is g–closed. Also $\{x\} = F \cap G$. Hence X is T''_D.

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ON $V-K_\lambda$ CURVES

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Abstract

Here $V-K_\lambda$ curves are defined on the hypersurface of a Riemannian space and some conditions under which a $V-K_\lambda$ curve becomes a $V-$indicatrix are discussed.

Let V_{n+1} be an $n+1$ dimensional Riemannian manifold, covered by coordinate neighbourhood $\{ y^\alpha ; U \}$ $(\alpha, \beta, \gamma, .. = 1, 2, ..n+1)$. Let V_n be an n dimensional hypersurface covered by coordinate neighbourhoods $\{ x^i ; U' \}$ $(i, j, k,.. = 1, 2, .. n)$ immersed in V_{n+1}. Let the immersion be given by $y^\alpha = y^\alpha(x^1, ..x^n)$. The rank of the matrix $\left[\dfrac{\partial y^\alpha}{\partial x^i} \right]$ is n. If the immersion is isometric then using the notations of Yano ([4] p. 88), the metrics g' and g of V_n and V_{n+1} respectively are related by

$$g' (X', Y') = g (BX', BY') \qquad ..(1)$$

where $X'=X'^h \partial_h$, $Y'=Y'^h \partial_h$, $\partial_h = \partial/\partial x^h$ are C^∞ vector fields in V_n, while $BX'=B_h{}^\alpha X'^h \partial_\alpha$, $BY'=B_h{}^\alpha Y'^h \partial_\alpha$, $\partial_\alpha = \partial/\partial y_\alpha$ are C^∞ -vector fields in V_{n+1} and $B_h{}^\alpha = \dfrac{\partial y^\alpha}{\partial x^h}$

Let N be a unit vector field in V_{n+1}, normal to V_n. i.e.

$$g (N, N)=1$$

and

$$g (BX', N)=0 \qquad ..(2)$$

for each vector field X' in V_n

Since B and N are linearly independent, any unit vector field λ, which is not normal to V_n, can be written as

$$\lambda = BS' + rN \qquad ..(3)$$

for some vector field S' in V_n and a function r on V_n. λ, being a unit vector field gives us $g'(S', S') = |S'|^2 = 1 - r^2$.

Let ∇ be a Riemannian connection in V_{n+1} and ∇' be a Riemannian connection in V_n, induced by ∇. Then according to Yano ([4] p. 90) the two connections are related as

$$\nabla_{BX'}BV' = B\nabla'_{X'}V' + h(X', V')N$$

where $h(X', V')$ is a symmetric tensor field of type $(0, 2)$ called second fundamental form of V_n. In particular if T' is the tangent field for the curve $\mathcal{C}$ then

$$\nabla_{BT'}BV' = B\nabla'_{T'}V' + \underset{V\ n}{K\ N} \qquad ..(4)$$

or

$$\underset{V\ A}{K\ W} = B\underset{V\ a}{k\ X'} + \underset{V\ n}{k\ N} \qquad ..(5)$$

where $\underset{V\ A}{K}$, called the associate curvature of V with respect to $\mathcal{C}$ (relative to V_{n+1}) and $\underset{V\ a}{k}$, called the associate curvature of V_n (relative to V_n), are the magnitudes of associate curvature vector fields $\nabla_{BT}BV'$ (relative to V_{n+1}) and $\nabla'_T V'$ (relative to V_n) respectively W and X' are unit vector fields in the direction of $\nabla_{BT}BV'$ and $\nabla'_T V'$ respectively. $\underset{V\ n}{k}$ is the normal curvature of the hypersurface V_n. V is an extension of the vector field BV', Squaring (5) we get

$$\underset{V\ A}{K^2} = \underset{V\ n}{k^2} + \underset{V\ a}{k^2} \qquad (6)$$

Now a curve say $\mathcal{C}$ in V_n, will be called a $V - K_\lambda$ curve, if at each of its point the unit vector field belongs to the plane determined by the associate vector fields $B\nabla'_T V'$ and $\nabla_{BT}BV'$, relative to V_n and V_{n+1} respectively, V being an extension of BV'. i.e. if

$$\lambda = aB\nabla'_T V' + b\nabla_{BT}BV'$$

Or using equation (4)

$$\lambda = (a + b)B\nabla'_T V' + b\underset{V\ n}{k\ N} \qquad (7)$$

Equating (3) and (7), we have

$$BS' + rN = (a+b) B\nabla'_T V' + b \frac{k}{V} \frac{N}{n} \tag{8}$$

Taking an inner product with $B\nabla'T'V'$, we find

$$g(BS' + rN, B\nabla'_T V') = g[(a+b) B\nabla'_T V' + b \frac{k}{V} \frac{N}{n}, B\nabla'_T V']$$

which, since B and N are linearly independent, reduces to

$$g(BS', B\nabla'_T V' = g[(a+b) B\nabla'_T V', B\nabla'_T V']$$

or using (1)

$$g'(S', \nabla'_T V') = (a+b) g'(\nabla'_T V', \nabla'_T V')$$

or

$$g'(S', \nabla'_T V') = (a+b) \frac{k^2}{V a} \tag{9}$$

Let θ be the angle between λ and N. Thus $r = \cos\theta = g(\lambda, N)$. Consequently $g'(S', S') = \sin^2\theta$. If β is the angle between the vector fields S' and $\nabla'_T V'$ then

$$g'(S', \nabla'_T V') = \frac{K}{V} \sin\theta \cos\beta$$

Equating this equation with (8), we get

$$(a+b) \frac{k}{V a} = \sin\theta \cos\beta \tag{10}$$

Now a curve with respect to which the vector field V is parallel in the sense of Levi-Civita, is called an indicatrix of the vector field V [1]. We shall call such a curve a V-indicatrix. We note that geodesics are self-indicatrices. A necessary and sufficient condition for a curve to be V-indicatrix is that associate curvature vanishes. So from (10) we have

Theorem 1 :

A $V - K_\lambda$ curve in V_n is V indicatrix if and only if,

(i) vector field λ is normal to V_n

or

(ii) vector fields S' is normal to associate vector field $\nabla'_T V'$

Now from (8) we get $r = \cos\theta = b \frac{k}{V n}$, which with equations

(6) and (10) gives us

$$(a+b)^2 \frac{K^2}{V A} = [(a+b)^2 - b^2 \cos^2\beta] \frac{k^2}{V n} + \cos^2\beta \tag{11}$$

From (10)

Theorem 2 :

If S' is any vector field which is not normal to $\nabla'_T.V'$ then a necessary and sufficient condition for a $V-K_\lambda$ curve to be V-indicatrix is that vector field λ is normal to V_n.

As a particular case we have,

Corollary-If S' is any vector field which is not normal to $\nabla'_T.T'$, the first curvature vector relative to V_n, then a necessary and sufficient condition for a self $-K_\lambda$ curve (called a K_λ curve by Tsagas [2]) to be a self indicatrix (geodesic) in V_n is that vector field λ is normal V_n

If a $V-K_\lambda$ curve is conjugate to the vector field V then $k_{Vn} = 0$, and using (6) and (11) we have.

$$(a+b) \; k_{Vn} = \cos \beta$$

equating this equation with (10) we find

$$\sin \theta = 1$$

if $\cos \beta \neq 0$. So

Theorem 3 :

If a $V-K_\lambda$ curve is conjugate to vector field V and if S is any vector field which is not normal to $\nabla'_T.V'$ then vector field is tangential to V_n As a particular case,

Corollary. If a self $-K_\lambda$ curve in an asymptotic line is V_n and if S' is any vector field which it not normal to $\nabla'_T.T'$ then vector field λ is tangential to V_n.

Corollaries of theorems 2 and 3 are more general than those proved by Upadhyay and Agnihotri [3].

Similarly we can define $V-K_\lambda$ curves in the Subspace of a Riemannian space. Results are being investigated.

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KERR-SCHILD CONGRUENCE AND SHEAR

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Abstract

The necessary and sufficient conditions for the Kerr-Schild congruence to be shear-free without the use of any field equations are studied.

It has been shown elsewhere [1] that for the Kerr-Schild metric

$$(1) \qquad g_{ij} = \eta_{ij} + 2H\psi_i\psi_j \quad \left\{ \begin{array}{l} i,\, j,\, .. \,= 1,\, 2,\, 3,\, 4 \\ \alpha,\, \beta,\, .. \,= 1,\, 2,\, 3 \end{array} \right\}$$

where η_{ij} is the metric of the Minkowski space-time in rectangular Cartesian coordinates, i.e. $\eta_{ij} = \text{diag}\,(-1,\, -1,\, -1\, +1)$, H is a scalar field and the vector field ψ_i is null and geodetic with respect to the Minkowskian metric, the Ricci tensor can be put in the form

$$(2) \qquad R_{\alpha\beta} = R_{44}\,\psi_\alpha\psi_\beta + C_\alpha\psi_\beta + C_\beta\psi_\alpha + A_{\alpha\beta},$$

$$(3) \qquad R_{\alpha 4} = R_{44}\,\psi_\alpha + C_\alpha$$

$$(4) \qquad R_{44} = \Box H - 2b_{,4} + K,$$

where

$$(5) \qquad C_\alpha = \Box(H\psi_\alpha) - \psi_\alpha\Box H + b_{,4}\,\psi_\alpha - b\psi_{\alpha,\,4} - b_{,\alpha}$$

$$(6) \qquad A_{\alpha\beta} = 2H\eta^{km}\psi_{\alpha,\,k}\,\psi_{\beta,\,m} - b(\psi_{\alpha,\,\beta} + \psi_{\beta,\,\alpha}) + b(\psi_\alpha\psi_\beta)_{,4}$$

$$(7) \qquad \Box = \eta^{ij}\frac{\partial^2}{\partial x^i\,\partial x^j}$$

$$(8) \qquad b = \dot{H} + H\theta$$

$$(9) \qquad \dot{H} = H_{,k}\psi^k$$

(10) $\qquad \theta = \psi^k{}_{,k}$

(11) $\qquad K = -2H(b' - H\psi^k \square \psi_k)$.

In writing the Ricci tensor in the form (2), (3), (4) we have in addition normalized ψ^l by the requirement.

(12) $\qquad\qquad \psi_4 = \psi^4 = 1$.

The curvature scalar R is given by

(13) $\qquad\qquad R = -2(b' + b\theta)$.

It has also been shown that the necessary and sufficient conditions for the Ricci tensor given by (2), (3) and (4) to satisfy the field equations.

(14) $\qquad\qquad R_{ij} = \tau \psi_i \psi_j$

τ being a scalar, are

(15) $\qquad\qquad C_a = 0$

(16) $\qquad\qquad A_{\alpha\beta} = 0$.

It is also well known that of the nine quantities C_a and $A_{\alpha\beta}$ only four are independent.

Consider now the expression for shear for the congruence ψ^l.

We have

(17) $\qquad\qquad 4\sigma^2 = (\psi_{i;j} + \psi_{j;i})\psi^{i;j} - \theta^2$

the semicolon indicating a covariant differentiation. Since ψ^l is null and geodetic we have

(18) $\qquad\qquad \psi_{i;j}\psi^{j;i} = -\dot\theta + R_{ij}\psi^i\psi^j$.

It is well known that for the metric (1) with ψ^l null and geodetic

(19) $\qquad\qquad R_{ij}\psi^i\psi^j = 0$.

Thus

(20) $\qquad\qquad \psi_{i;j}\psi^{j;i} = -\dot\theta$

From (17) and (20) we get

(21) $\qquad\qquad 4\sigma^2 = \psi_{i;j}\psi^{i;j} - \dot\theta - \theta^2$

It is easy to show that

(22) $\qquad\qquad \psi_{i;j}\psi^{i;j} = \eta^{\alpha\beta}\eta^{km}\psi_{\alpha,k}\psi_{\beta,m}$

and consequently (6) leads to

(23) $\qquad\qquad \eta^{\alpha\beta}A_{\alpha\beta} = 2H\psi_{i;j}\psi^{i;j} - 2b\theta$

or

(24) $\qquad\qquad \psi_{i;j}\psi^{i;j} = \dfrac{1}{2H}\cdot\eta^{\alpha\beta}A_{\alpha\beta} + \dfrac{b\theta}{H}$.

From (21) and (24) we find for shear the expression,

(25)
$$4\sigma^2 = \frac{1}{2H} \cdot \eta^{\alpha\beta} A_{\alpha\beta} + \frac{b\theta}{H} - \dot{\theta} - \theta^2.$$

Consider now the last three terms on the right hand side of (25) Substituting for b from (8) we have

(26)
$$\frac{b\theta}{H} - \dot{\theta} - \theta^2 = \frac{\dot{H}\theta - H\dot{\theta}}{H}.$$

Thus (25) becomes

(27)
$$4\sigma^2 = \frac{1}{2H} \eta^{\alpha\beta} A_{\alpha\beta} + \frac{\dot{H}\theta - H\dot{\theta}}{H}.$$

Let us now introduce an arbitrary function of $\frac{H}{\theta}$. Denoting it by g we have

(28)
$$g = g\left(\frac{H}{\theta}\right).$$

A dot differentiation then gives

(29)
$$\dot{g} = g' \cdot \left(\frac{\dot{H}\theta - H\dot{\theta}}{\theta^2}\right)$$

where

(30)
$$g' = \frac{dg}{du}, \qquad u = \frac{H}{\theta}.$$

It follows that

(31)
$$\dot{H}\theta - H\dot{\theta} = \frac{\dot{g}}{g'}\theta^2.$$

Substituting from (31) in (27) we get

(32)
$$4\sigma^2 = \frac{1}{2H} \cdot \eta^{\alpha\beta} A_{\alpha\beta} + \frac{\theta^2}{H} \cdot \frac{\dot{g}}{g'}.$$

This expression for shear can also be expressed in terms of R. For this purpose the expression for R is easily found from (2) and (4). It is given by

(33)
$$R = \eta^{\alpha\beta} A_{\alpha\beta} + 2C_{\alpha}\psi^{\alpha}.$$

Thus from (32) and (33) we get

(34)
$$4\sigma^2 = \frac{1}{2H}(R - 2C_{\alpha}\psi^{\alpha}) + \frac{\theta^2}{H}\frac{\dot{g}}{g'}.$$

It should be noted here that so for the only assumptions made have been that ψ^i is null and geodetic with respect to η_{ij} and $\psi_4 = \psi^4 = 1$. No field equations have been used. If we

are interested in field equations of the type (14) with τ equal to zero or otherwise, then, of course, we know that

(35)
$$R = 0, \quad C_a = 0, \quad A_{\alpha\beta} = 0.$$

Consequently

(36)
$$4\sigma^2 = \frac{\theta^2}{H} \cdot \frac{\dot{g}}{g'} \cdot$$

Thus we can state the following :

Theorem 1 : For the metric

$$g_{ij} = \eta_{ij} + 2H\psi_i\psi_j$$

η_{ij} being the Minkowskian metric in rectangular cartesian coordinates, H a scalar field and ψ^i being a null geodetic congruence with respect to η_{ij}, if

$$\psi_4 = \psi^4 = 1$$
$$R_{ij} = \tau\psi_i\psi_j$$

the congruence ψ^i is shear-free if and only if

(37)
$$\dot{g} = 0, \quad g' \neq 0.$$

In stating this theorem we have, of course, been guided by the Kerr and Vaidya solutions for each of which (15) (35), and (37) hold. But it is not necessary for (15) and (35) to be satisfied for the if and only if part of the theorem. It should be obvious from (32). We thus have the more general,

Theorem 2 : For the metric

$$g_{ij} = \eta_{ij} + 2H\psi_i\psi_j$$

η_{ij} being the Minkowskian metric in rectangular cartesian co-ordinates, H a scalar field and ψ^i being a null geodetic congu-ence with respect to η_{ij}, if

$$\psi_4 = \psi^4 = 1$$
$$\eta^{\alpha\beta} A_{\alpha\beta} = 0,$$

the congruence ψ^i is shear-free if and only if

$$\dot{g} = 0, \quad g' \neq 0.$$

In theorem 2 we have replaced the ten conditions (14) [which are actually equivalent to four independent conditions (15) and (16)] of Theorem 1 by a single condition,

(38)
$$\eta^{\alpha\beta} A_{\alpha\beta} = 0.$$

This is of course satisfied if $R = 0$ and $C_a = 0$.

The validity of theorem 2 does not require the vanishing of R. Consequently it would be worth while studying this case, i.e. studying solutions corresponding to the metric (1) for which the congruence ψ^l is null and geodetic with respect to the metric η_{ij}, $\psi_4 = \psi^4 = 1$ and ψ^l is shear-free but $R \neq 0$. One can also study solutions for which neither ψ^l is shear–free nor $R = 0$.

In stating both the theorems we have been guided by the known properties of the Kerr and Vaidya solutions. But that may not be the situation in general. The most general result we can state as a

Theorem 3 : For the metric

$$g_{ij} = \eta_{ij} + 2H \, \psi_i \psi_j$$

η_{ij} being the Minkowskian metric in rectangular cartesian co-ordinates, H a scalar field and ψ^l being a null geodetic congruence with respect to η_{ij}, if

$$\psi_4 = \psi^4 = 1$$

the necessary and sufficient condition for the congruence ψ^l to be shear-free is

(39) $$\eta^{\alpha\beta} A_{\alpha\beta} + 2\theta^2 \cdot \frac{\dot{g}}{g'} = 0.$$

An interesting consequence of Theorem 3 would be

Theorem 4 : For the metric

$$g_{ij} = \eta_{ij} + 2H \psi_i \psi_j,$$

η_{ij} being the Minkowskian metric in rectangular cartesian co-ordinates, H a scalar field and ψ^l being a null geodetic congruence with respect to η_{ij}, if

$$\psi_4 = \psi^4 = 1$$

the necessary and sufficient condition for the congruence to be shear-free is given by any one of

(*i*) $\eta^{\alpha\beta} A_{\alpha\beta} = 0,$

$$(ii)\ \dot{g}=0,\ g'\neq 0,$$

provided that the other one is satisfied.

Further investigations are in progress.

The author's thanks are due to Prof. P. C. Vaidya who in the course of discussions suggested the present investigation.

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AN ENZYMORPHOLOGICAL STUDY ON Mm. PECTORALIS OF SOME REPRESENTATIVE TYPES OF BIRDS

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Introduction

Avian Mm. pectoralis being a heterogenous muscle, its fibres have been classified into three main types, *viz.*, type I (red), type II (white) and intermediate on the basis of their contents of myoglobin, lipids, glycogen, oxidative and glycolyt c enzymes. George and Berger (1966). In all birds except category 6 of George and Berger (1966), the pectoralis muscle is a mixed muscle comprised of the above mentioned types of fibres in varying proportions. Muscles containing more of type I fibres are adapted for an ærobic metabolism and they metabolize fat as the chief energy fuel, whereas, the type II fibres utilize mainly glycogen as they are adapted for an anærobic metabolism to generate energy, George and Berger (1966), Bokdawala and George (1969), Grinyer and George (1969 ab), Pande and Blanchær (1971).

The metabolism of a muscle is dependent upon its cellular organization and biochemical components. The purpose of this study is to correlate structure with biochemical makeup with particular reference to some enzymes in the pectoralis muscle of a myna, a migra-

tory starling (Rosy Pastor), a Partridge and a lapwing. It may be mentioned that the choice of the bird species was made keeping in mind the fact that although some information is available on the former two birds of which one is migratory, very scanty reports are available on the Grey Partridge an important Indian game bird which is poor flier and the Redwattled Lapwing, a rather common bird with a slow flight. Hence this study was contemplated in some birds exhibiting different modes of flight.

Materials and Methods

The Mm. pectoralis of the following healthy adult birds was studied : All investigated birds were used at random.

1. Common Myna, *Acridotheres tristis* (Linnæus)
2. Rosy Pastor, *Sturnus roseus* (Linnæus)
3. Grey Partridge, *Francolinus pondicerianus* (Gmelin)
4. Redwattled Lapwing, *Vanellus indicus* (Boddært).

These birds were trapped alive in the field and supplied by local game dealers. In each bird, the fibre diameter of the different fibre types, their percentage distribution in addition to histochemical and biochemical analyses of succinate dehydrogenase (SDH) and alkaline and acid phosphatases were investigated as per techniques mentioned below. Lactate dehydrogenase (LDH) and glucose-6-phosphate dehydrogenase (G-6-PDH) were only localized histochemically.

Fibre types : The fibre types were determined on the basis of SDH staining (George and Berger).

Fibre diameeer : The diameter of the individual fibre types was determined using an ocular eye piece and a micrometer scale.

Percent distribution of fibres : The number of the fibres in percentage per unit area were calculated

SDH : Histochemical and quantitative : SDH activity was demonstrated histochemically by the method of George and Talesara (1961), using neotetrazolium as the hydrogen acceptor. The estimation of this enzyme activity was carried out according to the method of Kun and Abood (1949) and the enzyme activity expressed as μg formazan formed per 100 mg fresh weight / hour.

Alkaline and acid phosphatases : Histochemical and Quantitative : The alkaline and acid phosphatase activities were demonstrated histochemically by the method of Burstone (1961). The phosphatase activities were assayed in muscle pieces by the method of King and Armstrong (1934) using disodium phenyl phosphate as the substrate. The enzyme activities were expressed as King Armstrong units per 100 ml homogenate.

Lactate dehydrogenase (LDH) : Histochemical : The LDH activity was histochemically localized by the method of Pearse (1960) as adopted by George et al (1963).

Glucose-6-phosphate dehydrogenase : (G-6-PDH) Histochemical : The mitochondrial G-6-PDH was demonstrated by the method of Pearse (1960) and Nane and George (1965).

Results

The results are presented in Tables I and II.

Fibre types : All the birds investigated accept the Lapwing, possessed a mixed type of pectoralis with type I and intermediate fibres only. In the Lapwing however, type I and type II fibres were clearly discernible.

Fibre diameter : The largest type I and intermediate fibres were found in the Patridge and the least in the Rosy Pastor. The other two birds had fibres having diameter inbetween these two extremes (Table I).

TABLE I

Showing the percentage distribution and diameter of the different fibre types in the pectoralis muscle of the Myna, Rosy Pastor, Partridge and Lapwing.

Fibres		Myna	Rosy Pastor	Partridge	Lapwing
* Percent Distribution Unit Area of Fibres	Type I	58·89±3·19	84·44±0·88	11·55±1·1	79·31±0·88
	Intermediate	41·09±3·19	15·54±0·82	88·44±1·1	—
	Type II	—	—	—	20·67±0·75
@ Fibre Diameter (μ)	Type I	44·10±0·65	28·55±0·49	64·30±2·15	50·35±1·32
	Intermediate	77·00±1·80	45·41±0·90	39·30±2·25	—
	Type II	—	—	—	81·30±3·50
Specimens Used		4	4	3	3

*The values represent mean±S. E. of 10 readings.

The values represent mean±S. E. of 50 readings.

TABLE II

Showing the concentrations of SDH (μg formazan formed per 100 mg fresh weight/hour) and alkaline and acid phosphatases (King Armstrong units/100 ml. homogenate) in the pectoralis muscle of the myna, Rosy Pastor, Partridge and Lapwing

Enzymes	Myna	Rosy Pastor	Partridge	Lapwing
SDH	195.00±30.8	231.90±20.86	46.70±7.46	246.38±28.33
Alkaline Phosphatase	1.36±0.08	1.04±0.01	1.36±0.04	3.74±0.35
Acid Phosphatase	6.50±0.45	12.31±0.62	3.97±0.63	4.09±0.27

A minimum of four replicates were done for each enzyme and in all birds investigated and the data statistically analyzed.
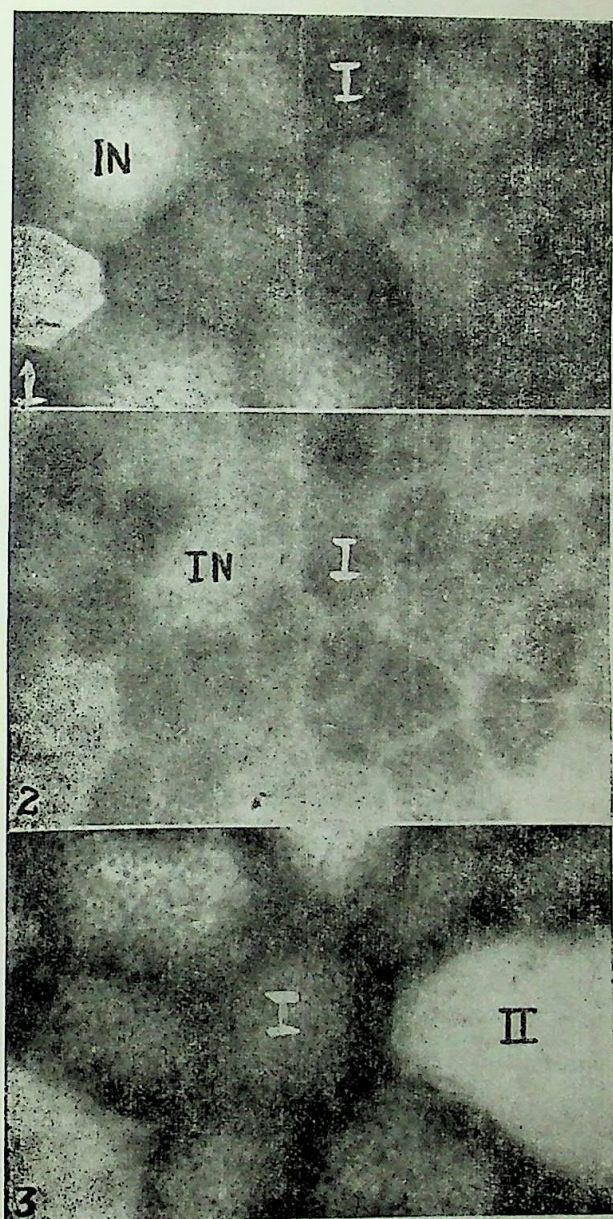
Figs. 1 to 3

T.S. of Mm. pectoralis of Myna, Rosy Pastor and Lapwing showing the localization of SDH activity. Note the higher enzyme activity in the type I (I) fibres as compared to either the intermediate (IN) or the type II (II). X 600.
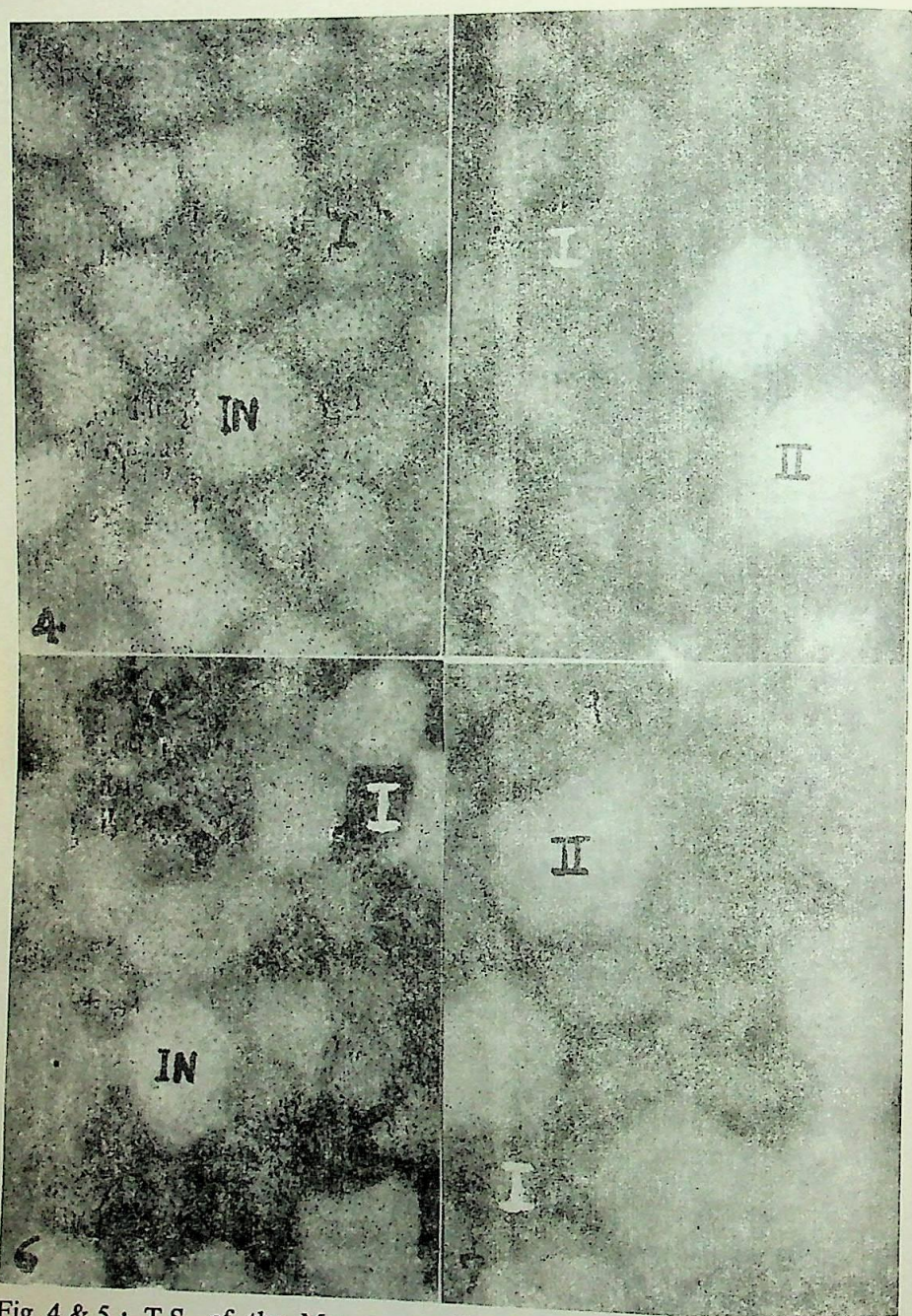
Fig. 4 & 5 : T.S. of the Mm. pectoralis of Myna and Lapwing respectively, showing the localization of G–6–PDH activity. The localization pattern is the same as for SDH. X 450.

Fig. 6 & 7: T.S. of Mm. pectoralis of Myna and Lapwing respectively showing the staining for mitochondrial LDH. Note the higher activity in the type I (I) fibres than the intermediate (IN) fibres of Myna and the type II(II) fibres of Lapwing X 450.

Percent distribution of fibres : The number of type I fibres in percentage / unit area were least in Partridge, highest in Rosy Pastor and followed in order by Lapwing and Myna. The intermediate / type II / type II fibres were maximum in Partridge and least in Rosy Pastor; Myna had more of these than the Lapwing. The latter had more type II fibres than the intermediate type in the Rosy Pastor but less than that in myna.

SDH : The histochemical localization of SDH was observed to be more in the type I fibres than in intermediate / type II ones in all the birds (Figs. 1 to 3).

Quantitatively, the lapwing pectoralis was the richest in SDH followed by rosy pastor and myna, while this enzyme was least in the partridge (Table II).

Alkaline and acid phosphatase : Any detectable phosphatase activity could be localized histochemically only on prolonged incubation. The activity appeared more in the type I fibres. The quantitative estimations however revealed highest alkaline phosphatase in lapwing, almost equal amounts in maya and partridge and least in rosy pastror (Table II). On the other hand, rosy pastor pectoralis was the richest in acid phosphatase. Myna had almost half the level of rosy pastor. Partridge and apwing possessed nearly same amounts of acid phosphatase (Table II).

LDH and G-6-PDH : The localization patterns of mito-chondrial LDH and G-6-PDH were exactly the same as SDH and was highest in type I fibres as compared to either the intermediate or type II fibres (Figs. 4 to 7).

Discussion

It has been pointed out earlier that the function of a muscle complements its structural components. Moreover, meta-bolism of a muscle depends on its cellular organization and biochemical makeup. It has also been shown (George and Berger, 1966) that the level of SDH activity in a muscle is an index of its capacity for oxidative metabolism. This point is further

illustrated by our study. Thus birds having more type I fibres (Lapwing and Rosy Pastor), possess higher SDH activity as compared to the others. The results could also be correlated with their respective modes of flight. Comparing values of Myna and Rosy Pastor, it is clear that although they belong to the same family (Sturnidae) and have similar fibre types in their pectoral muscles, yet the discrepancies in their content of SDH is marked. This is probably due to the fact that rosy pastor is a migratory starling and moreover, the birds were utilized in September/October, when they are in their premigratory phase and have increased oxidative metabolism, George and Berger (1966). Partridge on the contrary, is a member of the Galliformes, family Phasianidae, known for its flightless birds. Partridge is mostly a ground bird whose flight is short involving rapid wing beats. Thus, the least SDH in its pectoralis is justified. The Lapwing is an active flier with a slow flight but when pursued by other larger birds, it can swerve and mount into the sky rapidly, Dharmakumarsinhji (1955). The slow flight calls for an oxidative metabolism utilizing fat to obtain energy for muscular action George and Berger(1966), while the rapid mount would involve carbohydrate utilization, since, it has been shown that in the vigorously exercising muscle carbohydrate utilization predominates over that of fat Pande and Blanchaer (1971). Since these muscles are rich in LDH and G-6-PDH, it is evident that carbohydrate is utilized both by the glycolytic and the oxidative mechanisms i.e. hexose monophosphate shunt pathway. Further studies on levels of carbohydrates and enzymes involved in its metabolism in muscles of various birds are under way.

The alkaline and acid phosphatases though not clearly demonstrated histochemically in our study, have been localized in the sarcoplasmic reticulum of the red (type I) and white (type II) fibres of the pigeon pectoralis muscle and the dog diaphragm, Naik (1965), Vallyathan and George (1965). By virtue of their localization in the sarcoplasmic reticulum of the fibres, they would probably partake in interfibreal transportation

reactions involving the various metabolites. Thus transport of the glycogen from type II to type I fibres was suggested by George et al (1958). Recently, Ono (1970) has shown the presence of lysosomal type enzymes biochemically in bovine longissimus dorsi muscle. Thus on the basis of our biochemical results, on alkaline and acid phosphatases and Ono's (1970) work, the presence of lysosmes in avian muscle cannot be ruled out.

Summary

A histoenzymorphological study was carried out on the M_m. pectoralis of some representative types of birds. On the basis of fibre types, diameter, their percent distribution as well as on the levels of SDH, alkaline and acid phosphatases, LDH and G-6-PDH respectively, the muscle have been characterized as heterogenous muscle. The histophysiological makeup of the Mm. pectoralis has been correlated with the respective mode of flight of the birds investigated.

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EFFECT OF HYDROEN ION CONCENTRATION AND SALTS ON THE AMYLASE ACTIVITY OF THE LIVER OF LAEVICAULIS ALTE (FERUSSAC)

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Introduction

Due to the diversity in the diet, the mechanism of feeding and digestion is much more varied in the Gastropods than in the other group of Molluscs. The main contributors to the physiological investigations on digestion of Gastropods are Oshima (1932), Hashimoto and Onama (1949), Meenakshi (1954 & 1955), Huang and Giese (1958), Myers and Northcote (1958), Prosser and Vanweel (1958), Galli and Giese (1959) and Okada et al (1966). The present investigation only deals with the amylolytic activity in the liver of *Laevicaulis alte* (Ferussac), the common garden slug.

Material and Methods

The specimens were collected locally from their natural habitats. They were brought with moist earth in the laboratory and kept alive in the aquarium covered with wiregauge lid. Their feeding activities were observed in the laboratory.

Preparation of an enzymically active liver extract from Laevicaulis alte

The live specimens of *Laevicaulis alte* were dissected. The digestive tract was excised with maximum care. The liver mass was then removed and adhesive fluid surrounding it was removed with the help of the filter paper. It was washed in 0.6N saline. The surface moisture was removed by rolling a filter paper around it. It was immediately kept in the freezing chamber of the refrigerator in a wide tube. 40 to 50 animals yield about 2g. of liver mass.

Weighed liver mass (2g.) was ground to a fine state in a porcelain mortar along with pure roasted, acid free sand (10g.) and equal quantity of distilled water. The aqueous extract was transferred to a centrifuge tube for centrifugation for 20 minutes at 3500 r.p.m. The supernantant liquid was taken out carefully in a clean glass stoppered bottle and kept in the freezing chamber.

Method of study :

(a) General method of amylolytic experiment :

To study the activity of amylase two test tubes were taken. In the first 3 ml of 0.5 percent soluble starch and 0.5 ml of aqueous liver extract was added, while the second test tube was prepared as blank–with boiled aqueous extract of liver in which enzyme was destroyed. Both the tubes were kept in the incubator at 37°C. At a regular interval 0.5 ml of test mixture was withdrawn and tested with 1 ml of 0.0025M Iodine solution. The colour change was observed from blue, purple or colourless depending upon the presence of starch, erythrodextrin, or achroodextrin. The last two substances were formed by the digestion of starch. At the regular interval it was also compared with the blank (blue) to observe the difference.

In order to estimate relative enzyme activity under certain conditions, like the presence of various salts and pH, the time taken for the digestion of starch to reach achromic point, was noted. The reciprocals of the time taken to reach the achromic point are regarded in the expreriment representing as the relative activity of enzymatic action, and expressed in the terms of percentages of the fastest rate which will be relative activity (Rogers, 1940).

(b) Effect of salts on amyloclastic activity :

Action of potassium iodide, sodium chloride, sodium hydrogen phosphate, sodium sulphate and sodium nitrate salts were examined. In the blank insted of the salts, boiled aqueous liver extract was added. Test tubes containing 5.0 ml salt solution (0.5 M), 0.5 ml aqueous liver extract and 3 ml of 0.5 percent starch solution were incubated at 37°C. The periods of reaction were noted by examining the samples from the above tubes at regular interval and the time for reaching achromic point after adding each salt was noted separately. The rapidity of digestion

proceeded in the following successive order viz. in sodium chloride, potas·sium iodide, sodium nitrate, sodium sulphate, and no change could be detected in the blank and in sodium hedrogen phosphate. The results are shown in table I.

(c) Effect of Hydrogen ion concentration on amyloclastic activity :

Amyloclastic action was examined at pH 5.3, 6.2, 7.1 and 8.0 (phosphate buffers). The test tubes containing 5.0 ml of buffer, 3.0 ml of 0.5 percent starch and 0.5 ml of aqueous liver extract were incubated at 37° C. At regular interval the rapidity of digestion was examined by the use of iodine as mentioned before. The times taken to reach the achromic point were noted. The results are shown in the table II.

(d) General method of saccharogenic experiment :

The amount of sugar produced by the digestion of starch was measured. Test tubes containing buffer, enzyme and starch were incubated at 37°C. for a given period and then the sugar produced was estimated by Nelson–Somogyi method, Hawk, P. B. et al (1947). The buffers were similar to those used in the amyloclastic experiments. Test tubes containing 2 ml. of aqueous liver extract, 5 ml of buffer and 2 ml. of 5.0 percent starch solution were incubated at 37°C. for 17 hours after which the reducing sugar formed was estimated. The amounts are shown in the table III.

(e) Nature of sugar formed after digestion :

After incubating for 24 hours the product of digestion of starch by liver extract of *Laevicaulis alte* was examined for osazones to detect the nature of sugar.

Test tabes containing 10 ml of 5.0 percent starch and 10 ml of aqueous liver extract was incubated for 24 hours at 37°C. In this digested material, phenyl hydrazine hydrochloride and sodium acetate were added. This mixture was heated in boiling water bath for 20 m. minutes, cooled and then examined microscopically for osazones. The microscopic examination revealed glucosazones crystals, there by proving the nature of sugar formed to be glucose in the digestion of starch.

Discussion

Laevicaulis alte is a herbivorous slug feeding on vegetation. As there is a predominance of carbohydrates in its food, an efficient system for the digestion of carbohydrates is essential.

In the present investigation with reference to the effect of various salts on the activation of amylolytic process sodium chloride activated the amylolytic process to the maximum as compared to the effect of other salts. In contrast to the sodium chloride, sodium hydrogen phosphate was least effective. These results are in conformity with the results obtained by Wriggleworth (1928) in cockroach. Thus with the reference to the effect of salts, the amylase of *Laevicaulis alte* compares favourable with amylase of cockroach. In parasitic worms *Ascaris lumbricoides* and *Strongylus edentatus*, Rogers (1940). Sodium chloride activated the amylase action to a slight extant, but sodium hydrogen carbonate in case of *Ascaris lumbricoides* and potassium iodide in *Strongylus edentatus* activated the enzyme to the maximum amount. The contrast in the effect of salts on the amyloclastie activity in the parasitic mematodes and *Laevicaulis alte* indicates the different nature of amylase in all the three animals.

Hydrogen ion concentration is of great value for the relative velocity of the amyloclastic action of amylases. In the present investigation the optimum pH value for amyloclastic action of amylase from the liver of *Laevicaulis alte* worked out to pH 6.2, in which maximum amount of reducing sugar glucose was produced. In few gastropods and cockroach the pH value for amyloclastic action of amylase varies from 5.9 to 6.2, and in some parasitic worms it varies from 7.7 to 9.4. The value in *Pila virens* and *Melania crenulata*, Meenakshi (1954, 1955) is 6.0 and 5.9 respectively. In *Helix pomatia*, Myers et al (1958) it is 5.9. In parasitic worms *Ascaris lubricoides* and *Strongylus edentatus* the value for the optimum pH is 9.4 and 8.0 respectively, It will be observed from the above data that optimum pH value for amylase activity in *Laevicaulis alte* does not deviate much from the range of 5.9 to 6.2. The difference of pH value for amylase activity in case of parasitic worms further support the assumption that the amylase of all the three animals are distinct from each other, and are of different nature.

Summary

1. Amylolytic enzyme have been extracted from the liver of *Laevicaulis alte*. The saccharogenic and amyloclastic action of these enzymes have been examined in relation to the salts and hydrogen ion concentration.

2. Sodium chloride was fairly effective for amyloclastic action in *Laevicaulis alte.*

3. Amyloclastic and saccharogenic activity was greatest at pH 6.2.

4. Saccharogenic action on starch gave rise to glucose as identified by its osazones microscopically.

Acknowledge

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TABLE I

The effect of salts on the rapidity of carbohydrate digestion by aqueous liver extract of *Laevicaulis alte.*

Salts	Relative Amylolytic activity
Blank	Nil
Sodium hydrogen phosphate	very slow
Sodium sulphate	9.0
Sodium nitrate	24.0
Potassium iodide	37.0
Sodium chloride	100.0

TABLE II

The effect of hydrogen ion concentration on the relative activity of the amyloclastic action of amylase from the liver *Laevicaulis alte.*

pH	Relative Amyloclastic activity
8.0	20.0
7.1	37.0
6.2	100.0
5.3	58.0

TABLE III

Showing the amount of reducing sugar produced after the digestion of starch by aqueous liver extract of *Laevicaulis alte.*

pH	Reducing sugar mg./ml./wg.
5.3	5.0 mgs.
6.2	5.662 mgs.
7.1	4.40 mgs.
8.0	4.333 mgs.

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ON THE BASIC INTRUSIVE OF KUI
NEAR ABU ROAD, RAJASTHAN

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Abstract

This paper describes the basic intrusive of Kui area, Rajasthan. The basic magma intruded the calcareous metasediments of Ajabgarh series, Delhi system. A contact has developed between the basic intrusive and the country rock. This is particularly marked by the development of mineral wollastonite. Another interesting feature of the area is the occurrence of a small pocket of pyroxenite. The pyroxene-titanaugite-in some cases shows pseudouniaxiality. The field data suggest that the basic intrusive is older than the Erinpura granite.

Introduction

The area surrounding Abu Road town is occupied by mica schits, limestones, calc-gneisses and calciphyres with associated basic intrusives and Erinpura granite. The metasediments of the area form a part of one limb of a plunging isoclinal fold. From the field study it appears that the occurrence of mica-schists is scarce while calcareous metasediments cover a large area. Near Kui ($24° - 28' - 0''$ North Latitude and $72° - 48' - 30''$ East-Longitude) which is 1 km. to the east of Abu Road, gabbroic intrusion occurs within the calcareous metasediments.

The metasediments of the area have been referred to by Coulson as of Ajabgarh series, Delhi system. The igneous activity of the former Sirohi State may be summarized from Coulson's account as under : (*a*) Delhi basic rocks, (*b*) The Erinpura granite and its accompanying quartz reefs, aplites and pegmatites, (*c*) Basic rocks–post Erinpura granite but pre–Malani in age and (*d*) Malani system, post Malani basic rocks. Coulson described these rocks under a heading " Kui and Chandravati gabbors and dolerites." From a single chemical analysis and microscopic study, he concludes " The Chandravati rock is intermediate in nature between an olivine gabbro and a troctolite " (P. 81). It therefore appears that Coulson has either not described the basic rocks of Kui or has presumed them to be of the same composition as those of Chandravati which is hardly 7 kms. (4 miles) south of Kui. This note is therefore intended to present a detailed account of the rocks of Kui.

Structural Features

Topographical features of Kui area are interesting. The calcareous metasediments form prominent ridges. The western ridge trends NE – SW which is followed eastwards by a N – S ridge and in turn by another ridge trending NE – SW. Thus the calcareous metasediments occur as V – shaped outcrops giving an impression of a plunging fold topography. The outcrops of the basic intrusion occur in the central depression between the first two ridges that form a V pointing towards north. Thus basic–intrusion is surrounded on three sides by calcareous metasediments.

To the south is a fairly large outcrop of granite with its apophyses penetrating the basic igneous mass. These are mainly small dykelets as well as veins of granite, aplite and pegmatite. Hence the granite is younger than the basic mass. These igneous rock types show no signs of metamorphism revealing that they intruded already metamorphosed sediments.

The calcareous rocks of the area show steep dips. A fault zone has been established by Coulson running NE – SW – parallel to the strike of the sediments. The occurrence of breccia and baked material substantiates this view. It is almost along this fault-zone that the basic magma found its way.

The area was mapped on a large scale to determine the nature of the intrusive body and its effects on surrounding country rocks.

Method of Study

The optical determinations of the minerals of troctolite, pyroxene-wollastonite rock and pyroxenite specimens were done on five axes universal stage. The modal analyses were carried out using a six-spindle integrating eyepiece.

Petrography

The igneous rock types observed in the area include troctolite, pyroxenite and pyroxene–wollastonite rock.

Troctolite :

The rock composing the basic intrusion of the area is troctolite. The specific gravity (14 troctolite samples were tested) ranges from a minimum 2·75 to a maximum 2·95.

In the field, troctolite occurs as detached small masses in low grounds separated by patches of residual soil.

It extends for $\frac{1}{2}$ km. north-south and about $\frac{1}{4}$ km. east west. Field studies suggest that the basic magma was emplaced along the steeply inclined stratification planes of the metasediments. The absence of any sort of metamorphism in the intrusive mass suggests that it came after the sediments were folded. Since the basic intrusions of Kui and Chandravati are along the same strike, it is inferred that the two separately placed bodies may be the parts of one intrusive.

Troctolite shows a bluish hue and has pitted appearance. The latter may be the result of the removal of calcite which is observed in the slides of contaminated troctolite. Where it

GEOLOGICAL MAP OF KUI AREA (NOT TO THE SCALE)

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abuts against calcareous metasediments a concordant contact is distinctly visible. Within a very short distance troctolite disappears and the calcareous metasediments appear once again. Troctolite may, therefore, be taken to have intruded the calcareous metasediments.

In thin sections the rock· shows coarse grained hypidiomorphic texture. In some cases subophitic to poikilitic relations amongst the constituents (olivine and plagioclase) are observed.

Plagioclase (An 55–An 63) occurs as colourless to turbid rectangular laths with one or two sets of cleavages. In some sections they show distinct evidences of micro–faulting (Photograph-1), bending of twin lamellae (Photograph–2), and are also seen shattered by veinlets of iron ore or calcite.
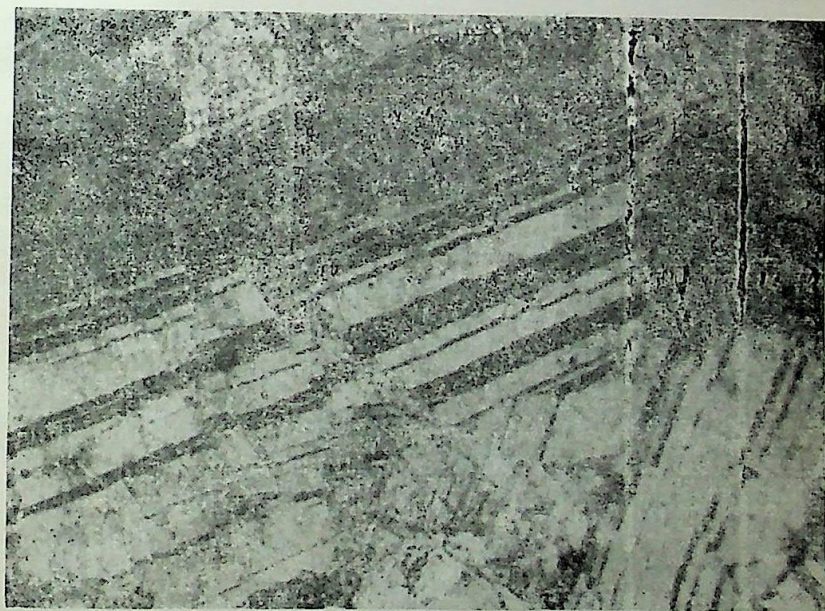
Photograph–1

Olivine is the next abundant constituent. It is fresh colourless with hexagonal outline ($2V_x = 80° - 84°$, – ve).

The composition of olivine varies from Fo 65 to Fo 75. When altered it has developed serpentine or brown antigorite or iron ore leaving behind its hexagonal form. Reaction rims

Photograph–2
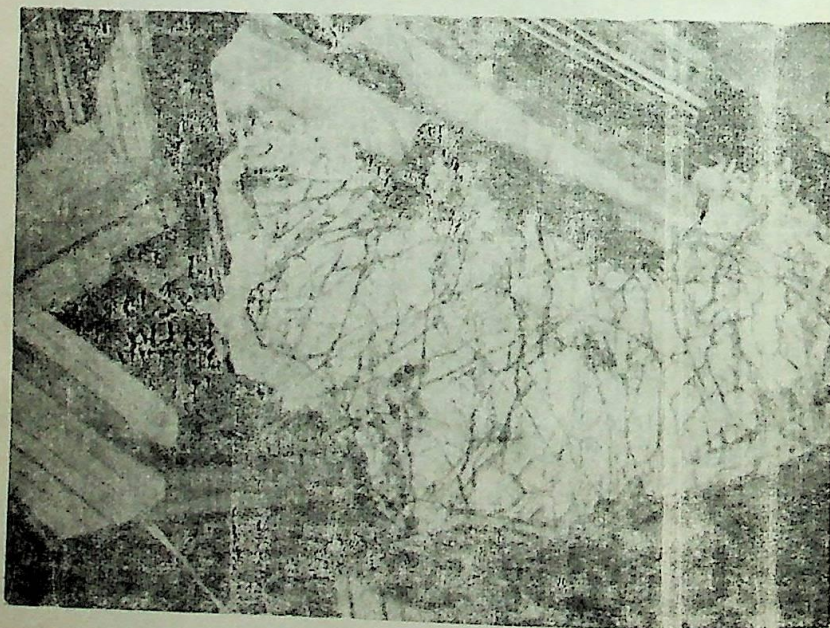
Photograph–3

of rhombic pyroxene (Enstatite) at the periphery of olivine are
noticed in some cases (Photograph No. 3). .

Titanaugite, diopsidic augite and biotite are present in
subordinate amount. Apatite and magnetite are the accessories
present.

Following is an average of five modal analyses :

Plagioclase	..	70·36 %
Olivine	..	24·12 %
Augite	..	2·25 %
Rest	..	2·11 %
Voids	..	1·32 %
		100·16

Pyroxenite :

It occurs in form of a small pocket at the southern edge of
the contact and as veins in troctolite. It is almost pure pyroxene-
titanaugite—with extremely coarse hypidimorphic texture having
black colour. It is feebly—pleochroic in shades of purple. It
occurs as prismatic sections with one set of cleavage. The
sections are also traversed by cracks. The mineral has altered
to green pleochroic hornblende with one cleavage and oblique
extinction ($8° - 15°$). Titanaugite has $n\beta = 1·699 \pm 0·002$ and
$2E = 62°$. It shows oblique extinction and the angle varies from
$37° - 45°$ ($Z \wedge C$). The most important feature of this pyroxene
is its pseudouniaxiality which is observed in some cases and may
be attributed to high titanium content.

Other constituents are diopside, microcline, orthoclase and
calcite.

Pyroxene—wollastonite rock :

The rock may be termed a contact rock formed as a result
of the contact of troctolite with the calcic sediments. The rock
shows crystalline texture with a variation in grain size right
from fine grained to coarse grained. In the field the rock occurs

as blocks giving a metallic sound when struck with hammer. The rock shows peculiar weathering in which pyroxene crystals occur as projections giving a rough aspect to the surface. The chief constituents are titanaugite, wollastonite and diopside.

Wallastonite, occurs as silky white fibrous crystals. Under microscope it is seen as colourless rectangular sections with one set of perfect cleavage. Some sections show oblique extinction ($22°$ to $30° - X \wedge C$) while others show parallel extinction. It is biaxial negative with $2E - 40°$.

Titanaugite under microscope shows a great variation in the body colour from faint to dark purple, schiller plates of magnetite, pseudo-uniaxiality in some cases, variation in extinction angle and $2E = 56° - 62°$.

Diopside occurs as colourless to pale green rectangular sections with one or two sets of cleavages. The extinction angle $Z \wedge C$ varies from $30° - 45°$. It is biaxial positive with $2E = 60°$.

In addition the rock also contains plagioclase, microcline, quartz, clacite and chlorite.

The preliminary study of the basic intrusive of the Kui area has brought to light the following facts :

1. Field data suggest that the basic intrusive is older than the Erinpura granite occurring quite close to it.

2. Development of a coarse—grained pyroxenite pocket in contact with calc sediments.

3. It appears that the intruding magma was troctolite. Formation of a small pocket of pyroxenite may therefore be assumed to be a product of magma contamination with the country rock, calcic sediments.

4. Wollastonite has developed mainly in contact with calcic sediments and has formed pyroxene—wollastonite rock. Wollastonite develops into big size crystals and the rock then is coarse-grained. Fine-grained texture rock is also present. Diopside makes its appearence in the rock.

5. The presence of microcline, orthoclase and diopside in pyroxenite, and plagioclase, microcline, quartz and diopside in pyroxene—wollastonite rock is quite significant, and demands closer scrutiny.
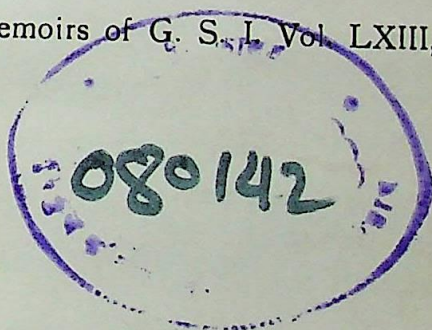
The area presents a fine study in limestone syntexis and hence the authors are pursuing in detail the optical, chemical and X-ray studies of the various minerals encountered in different rock types.

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